

ELECTRONIC STATES AND RESIDUAL CONDUCTIVITY IN RANDOM ALLOYS

By
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Department of Physics
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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ELECTRONIC STATES AND RESIDUAL CONDUCTIVITY IN RANDOM ALLOYS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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to the
Department of Physics
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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Dedicated to

MY PARENTS

CERTIFICATE

This is to certify that the work reported in this thesis entitled, "ELECTRONIC STATES AND RESIDUAL CONDUCTIVITY IN RANDOM METALLIC ALLOYS" has been carried out by PRABHAT KUMAR THAKUR under our supervision. No part of this work has been submitted elsewhere for a degree.

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NOTE

- 1) Several parts of the thesis have been published or have been accepted for publication.
 - (a) Chapter 3 (Section 3.3) has been accepted for publication in Journal of Physics F (awaiting for publication) under the title, "An Augmented Space Formalism for Electronic Density of States in $\text{Cu}_{1-c}\text{Ni}_c$ Alloy".
 - (b) Chapter 4 (Section 4.3.5) has accepted for publication in Journal Physics C; 18 (1985), 4677-4789 under the title, "Electrical Conductivity in Random Alloys".
- 2)
 - a) In Chapter 3 we have reviewed the old CPA theories (Kirkpatrick, Velicky and Ehrenreich-1970; Stocks Williams & Faulkner - 1971) of density of states in random alloys to point out the fine structures in the impurity subband in density of states within 2CPA for the same system.
 - b) In Chapter 4 we have reviewed the CPA work in static conductivity by Velicky (1969) and Brouers and Vedyayev, (1972), Niizeki (1977), Niizeki and Hoshino (1979) to give a consistent picture regarding the development of the theory of conductivity in random alloys.

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SYNOPSIS

The problems of electronic states and electronic transport in disordered alloys are a matter of interest for a long time both from theoretical and experimental point of view. Basically the electron or lattice wave propagation in a disordered solid is considered as a succession of elementary scatterings on the random atomic scatterers which are averaged over all configurations of atoms. For a real system in principle we have infinitely large number of configurations and so direct averaging is almost an impossible task in reality. Taylor and Soven (1967) first solved the problem by transforming the system of random scatterers by an effective medium through self-consistent choice of an effective scatterer which replaces each of the random scatterers in the frame-work of multiple scattering theory. The effective medium is determined corresponding to the choice that the single scatterer embedded

therein should produce no extra scattering on the average. The site energy corresponding to this effective medium determined for a site diagonal Hamiltonian in the frame-work of single site scattering theory is known as co-herent potential (CP).

The co-herent Potential Approximation (CPA) neglects the scattering from statistically coupled clusters of random scatterers. In situation of strong scattering where off-diagonal disorder is strong or both the diagonal and off-diagonal disorder are strong the need to go beyond single site CPA is very crucial. The difficulty in self-consistent generalisation of CPA suitable for describing multiple scattering from a cluster of random scatterers has been recognised for sometime. The difficulty was two-fold firstly the summation of appropriate scattering diagrams from various sizes of clusters is very cumbersome and secondly the simplified approximation made to make the problem tractable prior to configuration averaging leads to unphysical results because of the non-analytic character of the approximate Green Function. The self-consistent approximation appropriate for describing cluster effects known as cluster Co-herent Potential Approximation (CCPA) in the frame-work of Augmented Space Formalism (ASF) introduced by Mookerjee (1973) has been very successful for various realistic model systems.

The Augmented Space Formalism (ASF) ensures the essential Herglotz Property of Green Function so that the

reality of eigen energies, positivity and single valuedness of density of states are retained. This Formalism has been discussed in detail in Chapter 2. ASF coupled with the Recursion Method introduced by Haydock, Heine and Kelly (1972) form the practical basis for calculating density of states. The results of self-consistent cluster calculation of a single orbital model on the diamond and b.c.c. lattices have been reported earlier. Calculation of electronic density of states of valence bands in CCPA via ASF has been also performed previously for random III-V semiconducting alloys, e.g. $\text{Ga}_c\text{In}_{1-c}\text{As}$ (V.K. Srivastava, Ph.D. Thesis, 1982). In this work we report the calculation of density of states for metallic systems $\text{Cu}_1\text{-}_c\text{Ni}_c$ here in Chapter 3. The special features that emerge because of effects of cluster and off-diagonal disorder have been discussed in detail also in Chapter 3. It is argued that the impurity band has got sharp structures compared to the CPA which is true for all concentrations. The basic inputs are band parameters appropriate for Cu and Ni which are taken from reliable band structure calculations and the Recursion coefficient generated for 3d f.c.c. lattice of finite size configuration.

Regarding the electronic transport, residual conductivity is a matter of primary interest for disordered solid. Electrical conductivity for a random alloy has been formulated by B. Velicky (1969) in the single-site CPA based on the Kubo-Greenwood Formalism. Brouers and Vedyayev (1972)

have made application of this to a s-d system for semielliptic bands. Generalisation of conductivity by incorporating off-diagonal disorder has been done by Niizeki (1976,1977) but in the spirit of CPA. The aim of our present work is to develop an explicit formalism for calculating the conductivity in CCPA within ASF. Just as the Herglotz property is essential for any physically meaningful approximation for the one particle propagator for any approximation for the response function the vertex correction must satisfy Ward Identity so that the averaged macroscopic conservation laws are not violated. Bethe-Salpeter equation together with Ward Identity with both diagonal and off-diagonal self-energies form basis of calculation of conductivity. The conductivity formulation in CCPA via ASF is discussed in detail in Chapter 4.

The conductivity results for a model simple cubic lattice with strong off-diagonal disorder is shown in Chapter 4 to be very sensitive to the randomness in current and the vertex correction. Finally we have also reported the conductivity calculation for $\text{Cu}_{1-c}\text{Ni}_c$ for realistic band parameters of Cu and Ni taken from reliable band structure calculations. For $\text{Cu}_{1-c}\text{Ni}_c$ vertex correction is important but current correction is not appreciable because the widths of Cu and Ni d-bands are very close.

CHAPTER 1

INTRODUCTION

During the period of the late nineteen sixties and seventies, the problem of electronic states in disordered metallic alloys received attention of solid state theoreticians with the application and extension of the pioneering work of Coherent Potential Approximation (CPA) by Soven (1967). Kirkpatrick et al. (1970), Stocks et al. (1971) etc.. Soven first gave the single-site CPA theory with the idea of introducing complex site energy (or potential) which characterises the effective medium in a self-consistent manner within multiple scattering formalism. Later on Velicky (1969), and Brouers and Vedyayev (1972) carried out the theory of electrical conductivity in substitutionally disordered systems within single-site CPA starting from Kubo-Greenwood conductivity expression (1957, 1958).

The validity of single-site CPA theory has been recognised through application to various model systems as well as to realistic model Hamiltonians suitable for disordered metallic alloys. Kirkpatrick et al. (1970) made application to Ni-rich $\text{Ni}_{1-c}\text{Cu}_c$ and Stocks et al (1971) did the same calculation for Cu-rich $\text{Cu}_{1-c}\text{Ni}_c$ alloys for studying electronic density of states. Their results of electronic density of states was in good agreement with

the experimental density of states results by Seib and Spicer (1970) and Hufner et al (1973).

Brouers and Vedyayev (1972) extended the theory of conductivity by Velicky in the spirit of CPA to a model s-d Hamiltonian with a view to study the effect of s-d hybridisation on the residual resistivity. Their model calculations show the qualitative agreement of Mott's prediction of the deviation of Nordheim's rule due to the strong s-d hybridisation effects. In this way, single-site CPA theory was applied to study the nature of the electronic states and transport properties for disordered metallic alloys like $\text{Ag}_{1-c}\text{Pd}_c$, $\text{Cu}_{1-c}\text{Ni}_c$ etc. for tight binding Hamiltonians.

Ehrenreich and Schwartz (1976) remark that the CPA is a mean field theory analogous to the Weiss theory of magnetism, the random phase approximation (RPA) for describing Coulomb interactions in many electron system, or the Vander Waals theory of liquid gas system. While these theories are rigorously valid for only a limited range of characteristic parameters (for example, very high electron densities in the case of the RPA), they often provide physically reasonable and, indeed, semiquantitative descriptions in regimes substantially outside their region of validity. The same is true for the CPA.

Single-site CPA theory has the following drawbacks:

(i) it takes exactly into account only single-site

scattering and correlated scattering from cluster is not accounted for,

- (ii) the effect of potential fluctuations is automatically suppressed while doing such an average
- (iii) it can not properly take into account the off-diagonal disorder in the Hamiltonian, and
- (iv) the vertex correction (i.e., back-scattering effects) vanishes as an artifact of short-ranged potentials in single-site CPA.

The most obvious extension of the theory to overcome these limitations is to go beyond the single-site approximation by doing a general formalism so that the effects of scattering from statistically coupled cluster of various sites and that of the off-diagonal disorder could be included. Nickel & Krumhansl (1971) tried to make such generalisation using a method based on the corrected cumulant expansion to find electronic density of states of an one-dimensional model of an alloy. Butler (1972, 1973) also tried to calculate both the real and imaginary parts of the Green Function using a self-consistent cluster method. We will not try to describe these methods here, except to say that they are both intended to improve in the CPA by going beyond the single-site approximation through making application to one-dimensional tight binding models. Such a generalisation posed severe analytic problems

such as having discontinuities at various energies but even worse, they led to multi-valued density of states. Nickel and Butler (1973) speculated that since this non-analyticity had occurred in these calculations it might occur in many others.

It was pointed out by Haydock et al. (1972), Mookerjee (1973), Muller-Hartman (1973), Mills & Ratanavararaksa (1978) that for any real potential function the Green Function must have certain mathematical properties which are summed up by the statement that it is Herglotz. However, an approximation to the average Green Function will not be Herglotz, if it is obtained by ignoring contributions to it without regard to the preservation of this property. So if one makes such a level of approximation to Green Functions that Herglotzicity is lost, the nature of Green Function may lead to unphysical results like multivalued density of states or negative density of states etc. In order to get physical results Herglotzicity should be retained in any approximation to the Green Function. The fundamental difficulty with most theories that were proposed during the late 1960s and early 1970s as extensions of the CPA is that they lead to approximate Green Functions which are not Herglotz. It is now realised that the preservation of the Herglotz property must be one of the central considerations in the development of a theory which includes scattering from clusters, short-ranged order, off-diagonal

disorder, or the effects of positional disorder.

There have been attempts to include some of the effects of scattering from clusters of atoms, at least conceptually by using a technique called the molecular coherent potential approximation (MCPA) as discussed by Tsukada (1969) and Butler (1973). In fact, it is a straightforward generalisation of the CPA approach in which the lattice sites of the alloy are partitioned into cells that contain a number of sites, which is greater than one. Mathematically, it is obvious generalisation of the T-matrix equation in CPA. The effective self-consistent molecular scatterer is found by solving this T-matrix equations and used to calculate a Green Function. One can prove that the MCPA leads to a Herglotz Green Function within the same philosophy as that the CPA does. The main objection why MCPA is not a satisfactory theory is the imposition of fictitious unit cell boundaries and as a matter of fact the translational invariance is lost although it is invariant under cluster translations.

An approximation scheme for including the scattering from clusters that is very much easier to do calculations than the MCPA have been also proposed. This is known as embedded cluster method (ECM) as discussed by Inglesfield (1981), Baraff et al (1986) and references therein. The idea of ECM has been used by Gonis et al (1984) in $\text{Ag}_{1-c}\text{Pd}_c$ where they embedded the cluster in a CPA medium. The main

objection to the ECM is that "it is just a cobbled up theory in the sense that it is not a self-consistent theory like the CPA or even the MCPA" (Faulkner 1982).

All the above techniques described do not provide a reliable solution to the theoretical problem of developing a self-consistent theory of the electronic states of an alloy that goes beyond the single-site approximation. The problem of going beyond single-site CPA theory has been proposed by Mills (1978) in his original studies (known as Travelling Cluster Approximation) on the problem of a Herglotz average Green Function within the frame work of diagrammatic perturbation theory. But the problem is very cumbersome to evaluate the contributions of higher order terms for various sizes of cluster for a real three-dimensional lattice. Mills and Ratanavararaksa (1978) reported the density of states results for the three-dimensional (simple cubic) tight binding model of an alloy having diagonal disorder only in two-site travelling cluster approximation (TCA).

Mookerjee (1973a,b, 1975a,b,c) introduced a general formalism known as Augmented Space Formalism (ASF) to calculate configuration average of a general function of random variables by using abstract operator formulation of quantum mechanics. He was able to establish the idea of incorporating scattering effects from statistically coupled sites in a finite size cluster as well as the importance of

off-diagonal disorder in a self-consistent manner.

The formalism came out with success in producing Herglotz analytic Green Functions through applications to various model systems (Kaplan and Gray 1976, 1977, 1978; Kumar et al. 1982; V.K. Srivastava, Ph.D. Thesis, 1982; Kaplan et al. 1980; Thakur et al. 1986). Here, we, for the first time made application of ASF for the calculation of density of states of a disordered metallic alloy like Cu-rich $\text{Cu}_{1-c}\text{Ni}_c$ corresponding to the realistic choice of tight binding parameters from reliable band structure calculations for its constituents and using Recursion Method (Haydock, Heine and Kelly, 1972, 1975) to generate the local Green Function for d-bands. Results of density of states have been reported here in two-site CPA in ASF which shows sharp structures in the impurity band. Note that the fine structure in the cluster CPA (CCPA) density of states is a common feature which has been reported earlier by Kumar et al. (1982) in semiconducting alloys. The cluster CPA within ASF has been also applied for the calculation of vibrational properties of random transition metal alloys, e.g. $\text{Ni}_{1-c}\text{Pt}_c$, $\text{Ni}_{1-c}\text{Pd}_c$, $\text{Ni}_{1-c}\text{Cr}_c$ by R.P. Singh (1982), Mookerjee and Singh (1985).

So far ASF has been proved to be successful in dealing with either the calculations of electronic density of states or the vibrational density of states. It is a

general formalism in the sense that it can be applied to calculate configuration average of any physical observable which is a function of random variable provided that probability distribution corresponding to each random variable is known.

Another very important physical quantity of interest is the static residual conductivity. The theory of electrical conductivity in the strong scattering regime (beyond the Boltzmann limit) has been carried out by Roth (1975) and Singh & Roth (1982) for liquid metallic alloys in the effective medium approximation (EMA). The importance of back scattering effect has been recognised by them which was missed by Asano and Yonezawa (1980). The old CPA theories (Velický 1969; Brouers and Vedyayeb 1972) can not take into account the back scattering effects because of short-ranged potential used in the standard single-site CPA which leads to zero back-scattering effect on the average. Niizeki (1977a,b,c); Niizeki and Hoshino (1977) emphasized the importance of vertex correction (which characterizes the back-scattering effects) for long range potentials within a bond CPA type approach. They showed that static conductivity is very sensitive to the randomness of the current and the effect of vertex correction. The importance of vertex correction is discussed for multiple bands by Chitnavis and Raghavan (1983); Chitnavis & Leath (1983).

Following this we have developed a cluster CPA formulation within ASF by incorporating off-diagonal disorder and cluster effects from the statistically coupled sites for the evaluation of the configuration average of the Kubo-Greenwood conductivity expression. We have derived analytic representations for vertex correction as a function of CCPA Green Functions and self-energies. We have reported here the static conductivity results as an energy functional for a model simple cubic lattice with strong off-diagonal disorder. Finally, we also carried out the calculation of static conductivity as an energy functional in noble/transition metal alloy like $\text{Cu}_{1-c}\text{Ni}_c$ within two-site CPA.

In both the two cases it has been seen that vertex correction is not zero and the effect of randomness in current is appreciable for strong off-diagonal disorder.

CHAPTER 2

FORMALISM

2.1 Augmented Space Formalism

2.1.1 The Augmented Space Method:

The electron in a disordered solid experiences random potentials at the lattice positions and the system can have infinitely large number of configurations. The disorder in a solid is characterised by a set of hamiltonian parameters which are random variables and obey some probability distribution. So description of such systems should be from a statistical point of view and one hopes to describe the physical properties of the system through configuration averaging of the physical observables.

The augmented space formalism is an attempt to systematically take into account the configuration fluctuations while studying configuration averaging. The formalism is exact but for practical calculations approximations preserving constraints of physical origin may be generated. Augmented space formalism (ASF) was first introduced by Mookerjee (1973a, 1973b) and later on Kaplan and Gray (1976, 1977), Kaplan et al (1980) provided detailed exposition of this. The formalism has been proved to be powerful and efficient method for averaging quantities like one particle Green Function, Response Functions related to

two-particle Green Functions particularly when we want to go beyond the single site coherent potential approximation (CPA) and include effects of clusters, large off-diagonal disorder, short ranged order and so on. Previously ASF has been applied to average only Green Function as a single function of random variables. Here, our aim is to apply ASF to average physical quantity like static residual conductivity which involve products of more than two functions of random variables where direct decoupling is impossible.

2.1.2 Mathematical Form of ASF and its Application to Model Systems:

The detailed mathematics of ASF is carried out in various communications (Mookerjee - 1973; 1975a,b,c) Here we briefly discuss the main points related to the augmented space formalism to substitutional disordered system.

In a substitutional system the lattice sites are randomly occupied by the atoms of the type A,B,C etc. So the site energy e_i is a random variable which can take on value e_A, e_B etc. The random variable e_i will obey some probability distribution $p_i(e_i)$ such that $p_i(e_i) > 0$ and $\int_{-\infty}^{+\infty} p_i(e_i) de_i = 1$. One can say that the probability density is analogous to density of states of a solid in the sense that it is positive definite and while on integration should yield the number of electrons which can be normalised.

Mookerjee (1973) suggested that one can introduce a hypothetical space φ_i corresponding to a random variable e_i such that a basis set $\{|f_n^i\rangle\}$ and an operator M^i in that would characterise the random distribution of e_i . Note that the quantities $|f_n^i\rangle$, M^i and $p(e_i)$ are respectively the analog of eigenvectors, hamiltonian and density of states in a Hilbert space. Later on Mookerjee (1975) described $|f_n^i\rangle$ as the disorder field in analogy with a fermion/boson field and was able to give diagrammatic representation of it in a similar way as one does in Feynman diagrams for fermions or bosons. But here the problem is different because usually knowing the hamiltonian we want to find out density of states but here for a given probability distribution we have to find out an operator M^i corresponding to $p(e_i)$. Idea is the following, if $|f_0^i\rangle$ is a specially chosen member of the orthonormal basis $\{|f_n^i\rangle\}$ in φ_i then,

$$p_i(e_i) = -\frac{1}{\pi} \text{Im} \langle f_0^i | (eI - M)^{-1} | f_0^i \rangle \quad (2.1)$$

where $e = e_i + i \rightarrow 0^+$.

The problem can be handled in the analogous way to what one does in the continued fraction expansion of Green Function (Recursion Method; Solid State Vol.35 Haydock) in Recursion Method which we would discuss in the next section. One can try to find a convergent continued fraction of the probability density $p(e_i)$ of the following form

$$p(e) = -\frac{1}{\pi} \frac{1}{e - a_1 - \frac{b_1^2}{e - a_2 - \frac{b_2^2}{\ddots}}} \quad (2.2)$$

$e \rightarrow e + i0^+$

The operator M is tridiagonal matrix with a_1, a_2, a_3 etc. along the diagonal and b_1, b_2, \dots etc. along the off-diagonal positions in some basis $|f_n\rangle$. It should be noted that for some distributions like Lorentzian one can not get convergent continued fraction expansion. So the whole thing fails there. Let us choose our system to be a random alloy $A_c B_{1-c}$ for diagonal disorder (e_i) only. In the tight binding Anderson hamiltonian

$$H = \sum_i e_i p_i + \sum_{i \neq j} V T_{ij}, \quad (2.3a)$$

the diagonal term e_i form a set of random variables described by, $e_i = \{e^A N_i + e^B (1 - N_i)\}$ (2.3b)
 where $N_i = 0, 1$ for binary alloy.

If one neglects the short range order, probability density is given by,

$$\begin{aligned} p(N_i) &= c \delta(N_i - 1) + (1 - c) \delta(N_i) \\ &= -\frac{1}{\pi} \operatorname{Im}_{\eta \rightarrow 0^+} \left\{ \frac{c}{N_i + i\eta - 1} + \frac{(1 - c)}{N_i + i} \right\} \\ &= -\frac{1}{\pi} \operatorname{Im}_{\eta \rightarrow 0^+} \left\{ \frac{\tilde{c}}{N' - 1} + \frac{1 - c}{N'} \right\}, \quad N' = N + i\eta \\ &= -\frac{1}{\pi} \operatorname{Im}_{\eta \rightarrow 0^+} \frac{1}{N' - a_1 - \frac{c(1 - c)}{N' - (1 - c)}} \\ &= -\frac{1}{\pi} \operatorname{Im}_{\eta \rightarrow 0^+} \frac{1}{N' - a_1 - \frac{b_1^2}{N' - a_2}} \end{aligned} \quad (2.4)$$

where $a_1 = c$; $a_2 = (1-c)$ and $b_1^2 = c(1-c)$.

So M has (2×2) matrix representation

$$M = \begin{bmatrix} c & \sqrt{c(1-c)} \\ \sqrt{c(1-c)} & 1-c \end{bmatrix} \quad (2.5)$$

with eigenvalues 0 and 1. Its eigenvectors $|v_0^i\rangle$ and $|v_1^i\rangle$ describe occupancy states corresponding to the eigenvalues 0 and 1. Now we have to define general state vectors as for example $|f_0; r_i\rangle = |f_0\rangle \otimes |r_i\rangle$ in Augmented product space $\Psi = \sum x \pi \varphi_i$ and the average becomes,

$$\bar{F} = \langle f_0; r_i | \left[\int_{-\infty}^{+\infty} \{ \text{Im } G^{(M)}(h + i0^+) \} x \right. \\ \left. E(h) \cdot dh \right] | f_0, r_i \rangle \quad (2.6)$$

where $p(e) = -\frac{1}{\pi} \text{Im } G^M(h + i0^+)$.

If we want to generalise the augmented space for a set $\{e_i\}$ then $\Phi = \pi_i \otimes \varphi_i$. The basis in the product space is

$$|f\rangle = \{|f_i^1\rangle\} \otimes \{|f_i^2\rangle\} \otimes \dots$$

and if $g^{(M^i)}(z) = (zI - M^i)^{-1}$ then

$$P(\{e_i\}) = -\frac{1}{\pi} \text{Im} \langle f_0 | G(z) | f_0 \rangle \quad (2.7)$$

where $|f_0\rangle = |f_0^1\rangle \otimes |f_0^2\rangle \otimes |f_0^3\rangle \dots$

and $G(z) = g^{(M^1)}(z) \otimes g^{(M^2)}(z) \otimes g^{(M^3)}(z) \dots$

Let us consider the probability distribution for a single variable e

$$\begin{aligned}\bar{f} &= \int_{-\infty}^{+\infty} f(e) p(e) de \\ &= \int_{-\infty}^{+\infty} f(e) - \frac{1}{\pi} \operatorname{Im} g_{oo}^{(M)}(z) de \\ &\quad z \rightarrow e + i0^+\end{aligned}$$

$$\text{where, } p(e) = -\frac{1}{\pi} \operatorname{Im} \langle f_0 | g^M(z) | f_0 \rangle. \quad (2.8a)$$

Let us consider $f(z)$ a function of a complex variable z and has no singularities on the real axis in the neighbourhood of the branch cut of the function $g_{oo}^M(z)$.

$$\begin{aligned}\bar{f} &= -\frac{1}{2\pi i} \oint f(z) g_{oo}^M(z) dz \\ \text{or } \bar{f} &= -\frac{1}{2\pi i} \oint f(z) dz \langle f_0 | \int_{-\infty}^{+\infty} (z-h)^{-1} dp(h) | f_0 \rangle\end{aligned} \quad (2.8b)$$

where $g^{(M)}(z) = \int_{-\infty}^{+\infty} \frac{dp(h)}{z-h}$ and $p(h)$ is spectral projection operator of M .

$$\begin{aligned}\text{Thus } \bar{f} &= \langle f_0 | \int_{-\infty}^{+\infty} f(h) dp(h) | f_0 \rangle \\ &= \langle f_0 | \underline{f(M)} | f_0 \rangle\end{aligned} \quad (2.9)$$

where $\underline{f(M)}$ is the same function of M as f is of e . So we see that in general the average can be represented as a function

of the constructed operator M which involves the probability distribution.

2.1.3 Hamiltonian in ASF for Both Diagonal and Off-Diagonal Disorder:

Our starting hamiltonian is of tight-binding type

$$H = \sum_i \sum_n e_{in} P_{in} + \sum_{i \neq j} \sum_{n,m} V_{in,jm} T_{in,jm} \quad (2.10a)$$

$$\text{where } e_{in} = \{ e_{in}^A N_i + e_{in}^B (1-N_i) \}, \quad (2.10b)$$

i, j being site-indices and m, n band indices.

$$V_{in,jm} = V_{nm}^{AA} N_i N_j + V_{nm}^{BB} (1-N_i)(1-N_j) + V_{nm}^{AB} \{ N_i(1-N_j) + N_j(1-N_i) \} \quad (2.10c)$$

Here e_{in} represents diagonal disorder and $V_{in,jm}$ represents off-diagonal disorder arising from site energy and hopping integrals for the constituents A, B respectively.

$$p(N_i) = c \delta(N_i-1) + (1-c) \delta(N_i); N_i = 0, 1 \quad (2.11)$$

$$H = H_B + \sum_i \sum_n e_{in} N_i P_{in} + \sum_{i \neq j} \sum_{n,m} V_{nm}^{(1)} N_i N_j T_{in,jm} + \sum_{i \neq j} \sum_{n,m} V_{nm}^{(2)} (N_i + N_j) T_{in,jm} \quad (2.12)$$

where $e_n = (e_A - e_B)$, $V_{nm}^{(1)} = V_{nm}^{AA} + V_{nm}^{BB} - 2V_{nm}^{AB}$ and

$$V_{nm}^{(2)} = V_{nm}^{AB} - V_{nm}^{BB} \quad (2.13)$$

As before $M = \begin{bmatrix} c & \sqrt{c(1-c)} \\ \sqrt{c(1-c)} & 1-c \end{bmatrix}$ in the basis $|v_0^i\rangle, |v_1^i\rangle$.

$$(2.14)$$

The augmented space hamiltonian is

$$\begin{aligned} H = & H_B \otimes I + \sum_{n,i} e_n P_{in} \otimes M^{(i)} \otimes I^{(i)} \\ & + \sum_{nm} \sum_{i,j} V_{nm}^{(1)} T_{in,jm} \otimes M^{(i)} \otimes M^{(j)} \otimes I^{(ij)} + \\ & \sum_{n,m} V_{nm}^{(2)} \sum_{i \neq j} T_{in,jm} \otimes (M^{(i)} \otimes I^{(i)} + M^{(j)} \otimes I^{(j)}) \end{aligned}$$

I^i, I^{ij} being identity operators in all subspaces $\rho^{(k)}$ (2.15) except to those superscripted.

Until now we have not made any approximation. But the evaluation of Green Function in augmented space is very difficult because the large number of self-avoiding path which starts from some point and comesback to the same point. This problem is solved by Graphical Methods in conjunction with suitable forms of Green Function by the continued fraction representation of the Green Function through Recursion Method.

The Augmented space formalism is not just a mathematical way of averaging but one can analyse the cluster effects coming from statistical coupling of various components of the system. Before going to discuss its physical relevance to cluster co-herent Potential Approximation (CCPA) one should briefly discuss the Recursion and Graphical Methods

because we are going to use the to calculate density of states and conductivity of the system.

2.2 Graphical Method

2.2.1 Introduction:

In this section, by a graph we shall mean a set of 'vertices' connected by 'links'. The Graphical Method was first introduced by Haydock (1972) for calculation of resolvent. We would be using it to evaluate Green Function matrix element in augmented space and one sees the approximation made therein is related to cluster coherent Potential Approximation. A graph is associated with every basis in $\{|i\rangle\}$. To every element $|i\rangle$ of the basis set $\{|i\rangle\}$ is associated a vertex v_i and to each distinct pair of elements ($|i\rangle, |j\rangle$) a link or bond l_{ij} which may be directional (i.e. $l_{ij} \neq l_{ji}$). Suppose we want to invert the operator M then the contribution of each vertex v_i , is defined as $k(v_i) = \frac{1}{M_{ii}}$ and that of the link l_{ij} as a series of ordered vertices and links, i.e.,

$Q_N = \{v_i l_{ij} v_j \dots v_N\}$. Contribution of a path is defined as $k(Q_N) = \pi_{\text{vertices}} k(v_i) \pi_{\text{links}} k(l_{ij})$.

Now for $G = (z I - H)^{-1}$ the matrix element

$$\begin{aligned} G_{ij} &= \langle i | (z I - H)^{-1} | j \rangle \\ &= \sum_{N=0}^{\infty} \sum_{Q_N} \tilde{k}(Q_N) \end{aligned} \quad (2.16)$$

where Q_N are all self-avoiding paths from v_i to v_j . By a self-avoiding path we mean it does not trace any vertex more

than once inbetween two points for a given path.

2.2.2 CPA by Graphical Methods in Augmented Space:

In Augmented space the basis set $\{|nf_i^n\rangle\}$ contains two informations spatial extent of the lattice by n and $\{f_i^n\}$ the disorder field information. Now for a given probability density $p(e)$ of site energies of lattice points and considering only diagonal disorder in the hamiltonian one can write,

$$\tilde{H}_{nf,mf'} = \underline{M}_{ff'}^n \delta_{nm} + \underline{V}_{ff'} \quad (2.17)$$

$$p(e_i) = -\frac{1}{\pi} \text{Im} \langle f | (z \underline{I} - \underline{M}^i)^{-1} | f \rangle$$

$$|f\rangle = |f_0^1\rangle \otimes |f_0^2\rangle \otimes \dots \quad (2.18)$$

f being the ground state.

An electron at a site labelled by n and field state $|f_i^n\rangle$ can either make spatial hop to one of the near neighbours of the n th site with matrix element V keeping the field state same or it can remain in the spatial site while the field at the site n changes according as \underline{M}^i , the field at other spatial sites remaining the same. Suppose we want to find

$$G_{nm}(z) = \langle nf | (z \underline{I} - H)^{-1} | mf \rangle \quad (2.19)$$

The graph is shown in Figure(2.1a) for $G_{of,of}$ and for

$$M_{ij} = W_i \delta_{j,i+1}.$$

For an ordered system we have

$$P_{00}(z) = G_{00}(z) = \frac{1}{z - R_{00}(z)} \quad (2.20)$$

where $R_0(z) = \sum_i v_i^2 p_{ii}^{(0)}$, i 's are neighbours of zero and $R_0(z)$ is the contribution of all nonintersecting and self-avoiding paths from vertex 0 and back in the space. In the augmented space the configuration averaged Green Function $\bar{G}(z)$ can be written as,

$$G(z) = \frac{1}{z - R(z) - T(z)} \quad (2.21)$$

$R(z)$ is the contribution of all self-avoiding path from the vertex of and back that are either (a) entirely in the spatial part of the augmented space or (b) self-avoiding paths in the augmented space which include field hops but do not form closed loops. $T(z)$ is the contribution of all closed self-avoiding loops from 0f and back in the full augmented space connecting different spatial sites via field hops. Now in single site CPA we delink all $T(z)$ contributions.

Under this approximation, we have,

$$\begin{aligned} G^{DL}(z) &= \frac{1}{[z - R_0(z - W_1^2 G_1(z)) - W_1^2 G_1(z)]} \\ &= P_{00} [z - W_1^2 G_1(z)] \end{aligned} \quad (2.22)$$

which is clear from the graph shown in Figure (2.1~~9~~).

We have also,

$$G_i(z) = \frac{1}{z - R_0(z - W_1^2 G_1) - W_{i+1}^2 G_{i+1}(z)} \quad (2.23)$$

Now, in the conventional CPA, we have our self-energy $\Sigma(z)$ defined by

$$\begin{aligned} G^{CP}(z) &= \frac{1}{[z - \Sigma(z) - R_0(z - \Sigma)]} \\ &= P_{00}[(z - \Sigma(z))] \end{aligned} \quad (2.24)$$

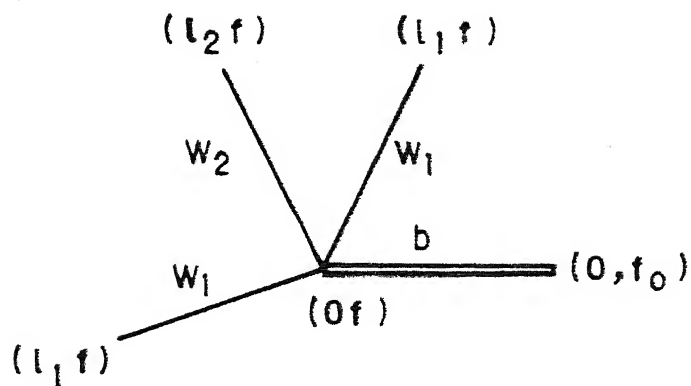
Equations (2.24) and (2.22) show the equivalence. Equivalence of the two has been discussed elaborately by Mookerjee 1974.

2.2.3 Cluster Coherent Potential Approximation (CCPA) in the Augmented Space by Graphical Methods:

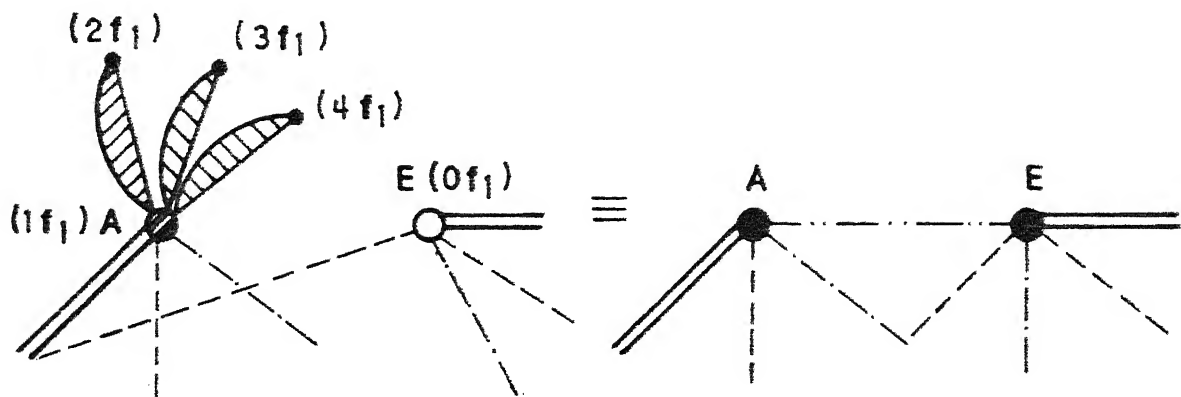
We have derived earlier the representation of the $M^{(i)}$ operator in disorder field space that characterises the probability distribution $p(e_i)$ in a basis $|v_0^i\rangle, |v_1^i\rangle$ in equation (2.5).




The corresponding operator representation of the hamiltonian in augmented space which couples the representation of the hamiltonian in the Hilbert space to the disorder field is also shown in equation (2.15).

We start from the configuration averaged Green Function,



(a)




 $= \sigma_0$
 $= \sigma_1$

Represents an octagonal decoration as in fig. 2.2 a,b

(b)

Fig. 2.1 (a) CPA Graph in ASF (b) Renormalisation of site end bonds of the octagon (2 CPA graph) in ASF due to the infinite medium

$$\tilde{G}_{in,jm}(z) = \langle \vec{r}_i n \tau^0 | (z \mathbb{I} - H)^{-1} | \vec{r}_j m \tau^0 \rangle \quad (2.25)$$

with $|\tau^0\rangle = \pi_i^x |v_0^i\rangle$, i, j being site indices and n, m being band indices. Note that upto this stage we have not made any approximation. We have discussed in the previous section that Green Function matrix element can be evaluated by graphical method and there is infact close connection between cluster CPA and the nature of the self-avoiding path that traces the solid from one point to the other in augmented space. In single-site CPA we have delinked all closed self-avoiding paths involving both spatial and field hops in the augmented space.

In a (n) cluster CPA only those self-avoiding non-intersecting paths will be taken into consideration which involve disorder field hops over the n -sites of the cluster. For a CCPA with (r_1, r_2, \dots, r_N) within the cluster all polygonal paths that do not completely lie in the subspace \mathcal{H} and involve those vertices and none other must also be exactly accounts for. These correspond to the multiple scattering within the cluster. Larger polygonal paths which involve sites within and without the cluster but which do not completely lie in the subspace \mathcal{H} , must be delinked and infact this is the approximation one makes to evaluate the configuration average of Green Function.

2.2.4 The Self-consistent Effective Medium in Augmented Space:

We have already discussed how in graphical theory one considers the CCPA corresponding to a given size cluster. So in graph theory one would be able to determine the self-avoiding polygonal path corresponding to the size of the cluster concerned. The polygonal self-avoiding path which takes into account the multiple scattering within the cluster is in fact immersed in the rest of the lattice and so the vertices and bonds (links) should be renormalised accordingly. Let us illustrate this by doing 2CPA for a random binary alloy. Corresponding to the 2-site cluster we have an octagonal decoration of self-avoiding polygonal path in the augmented space graph as shown in Figure (2.1a, 2.2a). The eight vertices of the octagon corresponds to the eight different configurations of the two-site cluster (2×2^2). The octagon belonging to a bond has no connection to another bond through the augmented space link. What it means is that the correlated scattering from three or more sites belonging to different bonds is ignored.

Finally we renormalize the vertices and bonds in the following way. The renormalization is a two-step process.

Step 1:

The decorating octagon is not an isolated octagon involving only the two spatial sites (0 and 1). If we look

at the vertex A ($1f_1$) and the bond AE ($1f_1$ to $0f_1$) belonging to the octagon is only one of the z bonds emanating from A to the z nearest neighbours of 1. The other remaining $(z-1)$ bonds (from $1f_1$ to $2f_1, 3f_1, \dots$ etc.) also hang on the site A. This is also true for other vertices (G, H, etc.) as well. So the whole octagon has to be renormalized due to the effect of the rest of the lattice in the augmented space representation. Once this renormalization is carried out let the whole octagon be now isolated. Mathematically the renormalised vertices $\sigma_0(z)$ and bonds $\sigma_1(z)$ are found as follows.

Suppose the whole lattice is divided into two subspaces: (i) An unrenormalised bond AE which we call system (1) It has a hamiltonian

$$H^{(1)} = V_2 (T_{AE} + T_{EA}) \quad (2.26)$$

and (ii) A lattice L which is the original lattice minus the link AE and in which all bonds and sites are renormalised by Σ . We call this to be the system (2). This has a hamiltonian

$$H^{(2)} = \Sigma_0(z) \sum_{i \neq A, E} P_i + \Sigma_1(z) \sum_{i, j \neq A, E} T_{ij} \quad (2.27)$$

Also there exists a linking hamiltonian,

$$H^{(int)} = \Sigma_1(z) \sum_i (T_{iA} + T_{Ai} + T_{iE} + T_{Ei}) \quad (2.28)$$

Now Green's operator corresponding to the subspace 1,

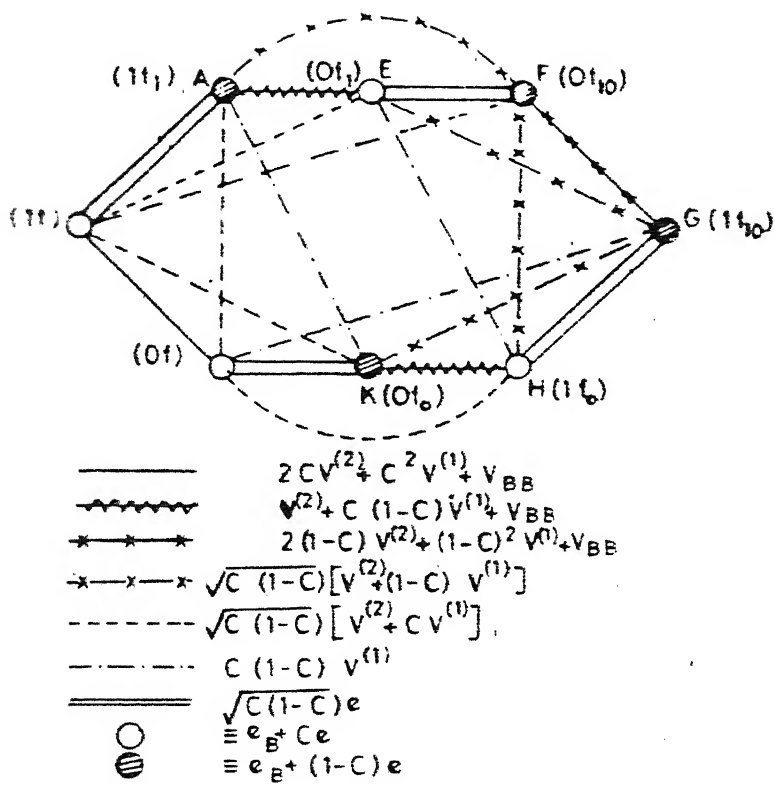


Fig. 2.2 (a)

$$G^{(1)} = \underline{P}_1 G \underline{P}_1 = [z I - H^{(1)} - H^{int} G^{(2)} H^{int}]^{-1} \underline{P}_1 \quad (2.29)$$

X^{-P}_Y = Inverse of the operator X in subspace Y

G = Green's operator in the total space, and

$$G^{(2)} = (z I - H^{(2)})^{-1} \underline{P}_2 \text{ with}$$

$$\underline{P}_1 + \underline{P}_2 = \underline{I} \quad (2.30)$$

The above equation immediately tells us that the effect of the rest of the medium on the bond AE is to modify the hamiltonian by

$H^{(1)} = H^{(1)} + \underline{\sigma}$ where the self-energy $\underline{\sigma}$ is given by

$$\begin{aligned} \sigma_{AA} &= \sigma_{EE} \\ &= \sigma_0(z) \\ &= \sum_1^2(z) \sum_{k,m \in N_A} G_{km}^{(2)} \end{aligned} \quad (2.31a)$$

$$\begin{aligned} \sigma_{AE} &= \sigma_{EA} \\ &= \sigma_1(z) \\ &= \sum_1^2(z) \sum_{k \in N_A} \sum_{m \in N_E} G_{km}^{(2)} \end{aligned} \quad (2.31b)$$

N_A = Nearest neighbour of A

N_E = Nearest neighbour of E.

Step 2:

Now as stated earlier that this isolated renormalised octagon has to be also renormalised because each of the vertices A,E has got connections with other vertices through either a field hop or spatial hop. This final renormalisation would be carried out in the following way. We divide the octagon into two subsystems a bond B(Of, 1f) and the rest of the octagon M. So that the system has the following hamiltonian representations, (see Figure 2.1b, 2-2a,b for renormalisation in graphical methods).

$$\underline{H}^B = \sum_{i,j} \sum_{\epsilon \in \text{Of}, 1f} \underline{H}_{ij}, \quad \underline{H}^M = \sum_{ij \neq \text{Of}, 1f} \tilde{\underline{H}}_{ij}, \quad (2.32)$$

$$\tilde{\underline{H}}^{BM} = \sum_{i \in B} \sum_{j \in M} (\tilde{\underline{H}}_{ij} + \tilde{\underline{H}}_{ji}) \quad (2.33)$$

Now, we have,

$$\begin{aligned} G^B &= \underline{P}_B G \underline{P}_B \\ &= [z I - \underline{H}^B - \tilde{\underline{H}}^{BM} G^M \tilde{\underline{H}}^{BM}]^{-P_B} \end{aligned} \quad (2.34a)$$

$$G^M = [z I - \underline{H}^M]^{-P_M} \quad (2.34b)$$

Now we have the final renormalised site $\Sigma_0(z)$ and bond $\Sigma_1(z)$ given by

$$\Sigma_0(z) = H_{00}^B + \sum_{j \neq 0} \sum_{k \neq 0} H_{oj}^{BM} G_{jk}^M H_{ko}^{BM}, \quad (2.35)$$

$$\Sigma_1(z) = H_{01}^B + \sum_{j \neq 0} \sum_{k \neq 1} H_{oj}^{BM} G_{jk}^M H_{k1}^{BM} \quad (2.36)$$

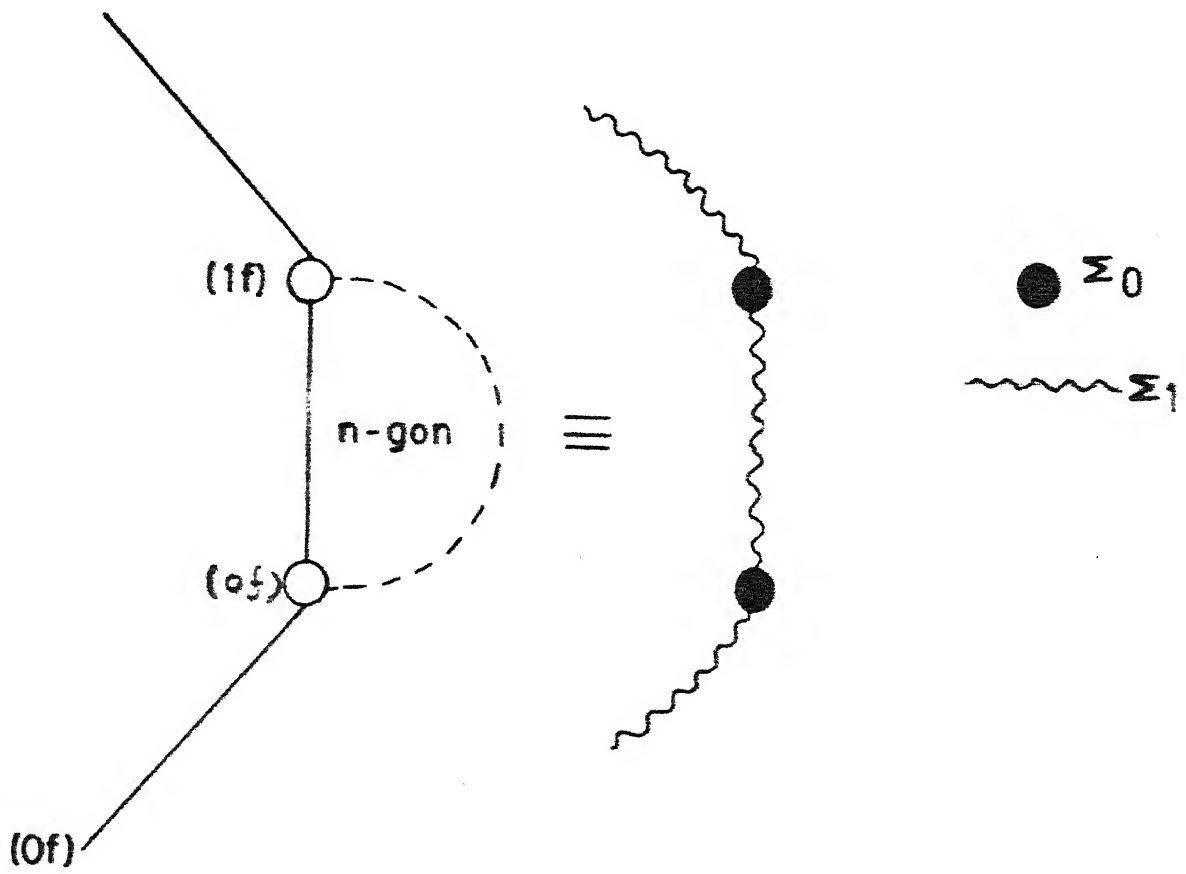


Fig. 2.2 b

Equations (2.35) and (2.36) are the set of self consistent form of equations which would provide self-consistent effective medium $= (\Sigma_{\Sigma_1}^0 \quad \Sigma_0^1)$. In the forthcoming chapter, we would make the application of 2CPA to $\text{Cu}_{1-c}\text{Ni}_c$ random substitutional alloy and discuss the physical effects of clustering coming from the statistical coupling of the two components of the system.

2.3 Recursive Solution of the Schrodinger's Equation

2.3.1 The Recursion Method:

The basic philosophy behind band structure like studies of the electronic structure in a solid is to exploit long range periodicity of the atomic potentials and to express the electronic properties of the solid as a coherent superposition of the electronic properties of all the atoms. But this is true when the interaction between electrons and atoms are not too strong. When the electrons interact strongly with the atoms this picture breaks down and properties no longer depend on long range periodicity but rather on only the first shells of neighbours of each atom. The d electrons in transition metals are prime examples of this regime. The physics is better understood by means of a solution that explicitly accounts for the role of local environment. Underlying physics in recursion (Solid State Ph. 35 (1980) - Haydock) is that the local orbital itself has the greatest effect and that successively more distant

orbital, have lesser effects.

The solution must therefore define a hierarchy of environments so that their relative influence is explicitly displayed in the local density of states. Physically, the local density of states is the intensity of each eigenstate on a particular atom or band. The local density of states for a basis orbital ϕ_0 is determined by the sequence of environments described by orthogonal states $\{u_n\}$ where $\{u_n\}$ is a linear combination of basis orbitals and u_0 is $\{\phi_0\}$. The $\{u_n\}$ must satisfy the condition that $H u_n = a_n u_n + b_{n+1} u_{n+1} + b_n u_{n-1}$.

H is the hamiltonian of the model and u_n are localised on the shell of atoms n hops from the atom accommodating ϕ_0 . The parameters a_n and b_n describe the coupling of each environment to itself and its neighbours. The aim of going over to such basis set is that one can transform any 3-dim model to pseudo-one-dimensional chain model where the chain is characterised by the parameters a_n and b_n the coupling constants of each environment to itself and its neighbours. As an example the local density of states for ϕ_0 can be written in terms of the parameters of the chain model as the continued fraction

$$n_0(E) = -\{\text{Im } 1/(E - a_0 - b_1^2/(E - a_1 - b_2^2/(E - a_2 - b_2^2/\dots)))\} / \pi \quad (2.38)$$

where $H_{nn} = a_n$, $H_{n,n+1} = H_{n+1,n}^* = b_n$.

Let us try to get the continued fraction for local density of states $n_0(E)$ starting from the Green Function. One can immediately check that in the above basis set $\{|u_n\rangle\}$ hamiltonian is a tridiagonal matrix

$$H = \begin{bmatrix} a_0 & b_1 & 0 & 0 & \dots\dots\dots \\ b_1 & a_1 & b_2 & 0 & \dots\dots\dots \\ 0 & b_2 & a_2 & b_3 & \\ 0 & 0 & b_3 & a_3 & \\ \vdots & \vdots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix}$$

$$G_0(E) = \langle \emptyset_0 | (ZI - H)^{-1} | \emptyset_0 \rangle$$

$$= \begin{bmatrix} (E-a_0) & -b_1 & 0 & 0 & \dots\dots\dots \\ -b_1 & (E-a_1) & -b_2 & & \dots\dots\dots \\ 0 & -b_2 & (E-a_2) & -b_3 & \dots\dots\dots \\ 0 & 0 & -b_3 & (E-a_3) & \dots\dots\dots \\ \vdots & \vdots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix}^{-1}$$

Let us define the determinant of the matrix with the first n rows and n columns deleted as $D_n(E)$.

$$\begin{aligned}
G_0(E) &= \frac{D_1(E)}{D_0(E)} \\
&= \frac{D_1(E)}{(E-a_0)D_1(E) - b_1^2 D_2(E)} \\
&= \frac{1}{(E-a_0) - b_1^2 \frac{D_2(E)}{D_1(E)}} \\
&= \frac{1}{E - a_0 - b_1^2 G_1(E)}
\end{aligned}$$

If we continue the process n steps we have, G_1, G_2, \dots, G_n .

$$G_0(E) = \frac{1}{E - a_0 - b_1^2 (E - a_1 - b_2^2 / \dots / (E - a_{n-1} - b_n^2 G_n(E)))} \quad (2.39)$$

where,

$$G_n(E) = \frac{1}{E - a_n - b_{n+1}^2 G_{n+1}(E)}$$

We see that $G_0(E)$ has continued fraction representation which in general may be very large in extent. It has been verified that for many systems the continued fraction converges. When the convergence is slow or poor it can be terminated by some termination schemes. So after doing reasonable level of recursion, for example 10 level is sometimes sufficient one uses termination scheme

as developed by C.M.M. Nex (1978, 1984), Haydock and Nex (1984).

2.3.2 Theory of the Continued Fraction Terminator:

Underlying philosophy for termination of the continued fraction for Green Function is that the approximate resolvent $R(Z)$ (which replaces G) should be such that the corresponding hamiltonian H should have the similar energy spectrum. By similar energy spectrum we mean it should correspond to as many as possible of the same singularities as the true hamiltonian H should have, i.e. band edges, Vanhove singularities etc. The continued fraction form of the Green Function for a uniform chain parameters, i.e. $a_n = a$, $b_n = b$,

$$G_0(E) = \frac{1}{E - a - b^2 G_0}$$

or

$$b^2 G_0^2(E) - G_0(E) (E-a) + 1 = 0$$

Therefore,

$$G_0(E) = \frac{(E-a) \pm \sqrt{(E-a)^2 - 4b^2}}{2b^2} \quad (2.40)$$

Here one sees that we need not have to use any termination scheme because the Green Function is exact. Now let us consider a general system having a single band hamiltonian. In this case square root terminator is appropriate as shown by Haydock and Nex (1984). Here, we illustrate its application

mathematically . We have the Green Function,

$$G(E) = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{\ddots - b_{n-2}^2} t(E)}} \quad (2.41)$$

where $t(E)$ = Required terminator.

Since an eigenstate of the chain is some linear combination of the states u_0, u_1, \dots ; we write the Schrodinger equation for the chain in the following form

$$H \sum_{n=0}^{\infty} p_n u_n = E \sum_{n=0}^{\infty} p_n u_n \quad (2.42a)$$

In matrix form

$$\begin{bmatrix} (E-a_0) & -b_1 & 0 & \dots \\ -b_1 & (E-a_1) & -b_2 & 0 & \dots \\ 0 & -b_2 & \dots & \dots \\ \vdots & \vdots & & \end{bmatrix} \begin{bmatrix} p_0 \\ p_1 \\ \vdots \\ p_n \end{bmatrix} = 0 \quad (2.42b)$$

The recursion co-efficients can be found in terms of orthogonal polynomials. We use those of first kind $p_i(E)$ and the second kind $q_i(E)$. Now making a proper choice such that

$$p_{-1} = 0 = q_{-1}, \quad p_0 = 1$$

$$\text{and } q_0 = b_0^2 \quad (2.43a)$$

$$\text{we have } p_{i+1}(E) = (E - a_i)p_i(E) - b_i^2 p_{i-1}(E),$$

$$i = 0, 1, 2, \dots, (n-2) \quad (2.43b)$$

$$\text{and for } i = 1, 2, \dots, (n-2)$$

$$q_i(E) = (E - a_i)q_{i-1}(E) - b_i^2 q_{i-2}(E) \quad (2.44)$$

One writes

$$G(E) = \frac{q_{n-2}(E) - b_{n-1}^2 t(E) q_{n-3}(E)}{p_{n-1}(E) - b_{n-1}^2 t(E) p_{n-2}(E)} \quad (2.45)$$

For a single band density of states

$$t(E) = [E - (\alpha + \beta)/2 - \sqrt{(E - \alpha)(E - \beta)}]/2b^2 \quad (2.46)$$

α, β are band-edges and

$$b = \frac{(3 - \alpha)}{4}.$$

For many band case trivial extension of this can be made as discussed by C.M.M. Nex(1984). The various possible

termination schemes has been discussed by Haydock and Nex (1984) and C.M.M. Nex (1984). Now-a-days Recursion Method is used to find local density of states for various ordered and disordered systems. The newly developed termination schemes have made the method very efficient.

CHAPTER 3

THE ELECTRONIC DENSITY OF STATES FOR METALLIC ALLOYS (TRANSITION/NOBLE METAL) IN CO-HERENT POTENTIAL APPRO- XIMATION (CPA) AND CLUSTER CO-HERENT POTENTIAL APPRO- XIMATION (CCPA)

3.1 Introduction

Soven (1967) first crystallised the idea of the co-herent Potential Approximation (CPA) for describing electronic density of states in disordered systems. Although the idea was not new. Self-consistent effective medium theories had been discussed in one form or another in different contexts: propagation of waves through disordered layers, dielectric response of insulators injected with conducting globules and so on. We should like to emphasize that the ideas behind the CPA and its cluster generalisations are a lot more general than the specific application here may suggest.

CPA has been applied to various disordered alloys and it is reasonably in agreement with experiments. The usual single-site coherent potential approximation arises from the self-consistent solution of the approximated multiple scattering equations. The approximation involves replacement of each of $(N-1)$ scatterers out of N scatterers by an effective potential such that there is no extra scattering on the average from the N th center representing the exact potential. Soven (1967) and Velicky et al (1968) made

application of CPA to various model systems. Our intention would be to generalise the CPA to include contributions from exact clusters self-consistently. The aim would be to apply the formalism to study the electronic density of states for disordered metallic binary noble metal/transition metal alloys. Calculations of density of states for Ni rich Cu-Ni alloys within the CPA frame work has been discussed by Kirkpatrick, Velicky and Ehrenreich (1970). Later on calculations on Cu rich Cu-Ni alloys have been shown by G.M.Stocks, R.W. Williams and J.S. Faulkner (1971) through trivial extension of the model by Kirkpatrick et al. (1970).

3.2.1 The CPA: A Recapitulation:

Let us recapitulate single-site CPA theory and its application to noble/transition metal alloys. We would be discussing the effective medium approach to derive the CPA equation. The well known tight binding hamiltonian for a single-band has the following form,

$$H = \sum_i \epsilon_i P_i + \sum_{\substack{i,j \\ i \neq j}} V_{ij} T_{ij} \quad (3.1a)$$

where, for binary alloy for example, $\epsilon_i = \epsilon_A, \epsilon_B$

ϵ_A, ϵ_B site energies of A, B

V_{ij} = Hopping integral corresponding to a hop from
ith site to jth site

T_{ij} = Transfer operator; P_i = projection operator

where i, j = site indices.

$$\text{More explicitly, } (p^2/2m + V_i^c)|i\rangle = \epsilon_i |i\rangle \quad (3.1b)$$

V_i^c = crystal potential corresponding to the i th site
and

$$V_{ij} = \langle i | \sum_{n \neq i} V_n^c | j \rangle \quad (3.1c)$$

Suppose the hamiltonian written in equation (3.1) has only diagonal disorder, i.e. ϵ_i is only random. Then underlying philosophy in single-site effective medium theory is that if any of the effective potential $\Sigma(z)$ (Coherent Potential) is replaced by an exact potential ϵ_i there would be no extra scattering on the average. Mathematically this means the average of the single-site scattering operator

$$\bar{\tau}_i(z) = (\epsilon_i - \Sigma(z)) / \{1 - (\epsilon_i - \Sigma(z)) \bar{F}(z)\} \quad (3.2)$$

vanishes, i.e.,

$$\langle \tau[\Sigma(z)] \rangle = 0, \quad (3.3)$$

where,

$$\Sigma(z) = \text{self-energy or Coherent Potential}$$

$$z = E + i0^+$$

and

$$F(z) = \text{Green Function for the alloy.}$$

$$\text{More explicitly, } \bar{F}(z) = F_0(z - \Sigma(z)) \quad (3.4)$$

F_0 represents the Green Function corresponding to the crystalline system. Equation (3.2) together with equation (3.4) constitute the self-consistent equation in single site

Coherent Potential Approximation which has the following form:

$$\frac{c (\epsilon_A - \Sigma(z))}{1 - (\epsilon_A - \Sigma(z)) \bar{F}(z)} + \frac{(1-c) (\epsilon_B - \Sigma(z))}{1 - (\epsilon_B - \Sigma(z)) \bar{F}(z)} = 0 \quad (3.5)$$

Equation (3.5) can be written in more convenient form as follows:

$$\Sigma(z) = \bar{\epsilon} + \frac{c(1-c) \bar{F}(z)}{1 - \{ (1-2c)\delta + (\bar{\epsilon} - \Sigma(z)) \} \bar{F}(z)} \quad (3.6)$$

where,

$$\bar{\epsilon} = c \epsilon_A + (1-c) \epsilon_B; \delta = \epsilon_A - \epsilon_B$$

We have made the assumption that the hamiltonian involve single-band parameters $\epsilon_A, \epsilon_B, V_{AA}, V_{AB}, V_{BB}$ etc. But this assumption is far from reality. A lattice site in a solid can have in general many orbitals or bands. For example in a system like $\text{Cu}_{1-c}\text{Ni}_c$, c being concentration, Cu-site or the Ni site have s and d bands both of which play significant role in its various physical properties magnetism, resistivity, specific heat etc. It has been pointed out by Hodges et al (1966) that the s-d hybridisation plays important role in transition and noble metals. So one should start with the density of states of the pure system where hybridisation is taken care of to do any realistic level calculation for such random systems.

Our aim would be to consider the general hamiltonian in which hybridisation effect is taken into account. The general hamiltonian of s-d noble/transition metal system has the following form:

$$\begin{aligned}
 H = & \sum_n |ns\rangle \epsilon_n^s \langle ns| + \sum_{m \neq n} |ns\rangle h_{nm}^s \langle ms| \\
 & + \sum_n |nd\rangle \epsilon_n^d \langle nd| \\
 & + \sum_{m \neq n} |nd\rangle h_{mn}^d \langle md| + \sum_n \gamma_n(x) [|ns\rangle \langle nd| \\
 & + |nd\rangle \langle ns|] \quad (3.7)
 \end{aligned}$$

$|ns\rangle$ and $|nd\rangle$ are Wannier state associated respectively with s and d band at the site n.

$\epsilon_n^{s,d}$ = Center of the s,d band

h_{nm}^s = Hopping term corresponding to s band

h_{nm}^d = Hopping term corresponding to d band

γ_n = Hybridisation parameter for s-d interaction.

In fact one can write down the matrix representation of H in the following form:

$${}^2H = \begin{pmatrix} H_{ss} & H_{sd} \\ H_{ds} & H_{dd} \end{pmatrix}; \quad \underline{\epsilon}_i = \begin{pmatrix} \epsilon_i^s & \gamma_i \\ \gamma_i & \epsilon_i^d \end{pmatrix} \quad (3.8)$$

The more explicit representation in terms of t_{2g} and e_g symmetry components of the d-band is given by,

$$\underline{H} = \begin{bmatrix} H_{ss} & H_{sd} & & \\ H_{ds} & H_{TT} & H_{TE} & \\ & H_{ET} & H_{EE} & \end{bmatrix} \quad (3.9)$$

It has been discussed by Ehrenreich and Schwartz (1976) that eventually all these would lead to a self-consistent CPA equation having the following matrix form:

$$\underline{\Sigma}(z) = \underline{\bar{\Sigma}} + c(1-c) \underline{\delta} \underline{\bar{F}}(z) [\underline{I} - \{ (1-2c) \underline{\delta} + (\underline{\bar{\epsilon}} - \underline{\Sigma}(z)) \} \underline{\bar{F}}(z)]^{-1} \dots \quad (3.10)$$

where $\underline{\delta} = (\underline{\Sigma}_A - \underline{\Sigma}_B)$; $\underline{\bar{\Sigma}} = c\underline{\Sigma}_A + (1-c)\underline{\Sigma}_B$ and \underline{I} = Unit matrix of (2x2) size. Here the energy parameters of the host B have matrix representation in s and d-bands. Explicit matrix representation for $\underline{\epsilon}_i$ is shown in equation (3.8).

The structure of the CPA equation (3.10) for the random binary alloy corresponding to the Hamiltonian in equation (3.7) is same as the CPA equation in (3.6). Only difference is that here the self-energy $\underline{\Sigma}(z)$ and the disordered alloy Green Function $\underline{\bar{F}}(z)$ appear in the form of matrices having (2x2) representations in s and d-bands. Here in matrix form we have self-energy and Green Function respectively given by the following expressions:

$$\Sigma(z) = \begin{bmatrix} \Sigma_o^s(z) & \Sigma_{sd}(z) \\ \Sigma_{sd}(z) & \Sigma_o^d(z) \end{bmatrix} \quad (3.11a)$$

$$\bar{G}(z) = \begin{bmatrix} \bar{G}_{ss}(z) & \bar{G}_{sd}(z) \\ \bar{G}_{ds}(z) & \bar{G}_{dd}(z) \end{bmatrix} \quad (3.11b)$$

where $\Sigma_o^s, \Sigma_o^d, \Sigma_{sd}$ are respectively the self-energies corresponding to the site-energies for s, d-bands and hybridisation parameter. It is very interesting to note that each of the Green Functions $\bar{G}_{ss}(z), \bar{G}_{dd}(z)$ and $\bar{G}_{sd}(z)$ having representations in s,d-band indices is functional of all the component self-energies. Now in the k-space we have, hybridised s and d-bands model Hamiltonian for the host, i.e., the crystalline system given by

$$H(\vec{k}) = \langle \vec{k} | H | \vec{k} \rangle = \begin{bmatrix} H_{ss}(\vec{k}) & \gamma_{sd} \\ \gamma_{ds} & H_{dd}(\vec{k}) \end{bmatrix} \quad (3.11c)$$

and $G(k, z)$ = Spectral Function for the Crystalline System

$$= \begin{bmatrix} G_{ss}(k, z) & G_{sd}(k, z) \\ G_{ds}(k, z) & G_{dd}(k, z) \end{bmatrix}$$

where more explicitly in band structure terms
we have, for crystalline system

$$\begin{aligned} G_{ss}(k, E) &= \frac{z - \epsilon_B^d - V_{dd}(\vec{k})}{\left[(z - \epsilon_B^s - V_{ss} S(\vec{k}))(z - \epsilon_B^d - V_{dd} S(\vec{k}) - \gamma_{sd}^2) \right]} \\ &= \frac{z - \epsilon_B^d - V_{dd}(E_s(\vec{k}) - \epsilon_B^s)/V_{ss}}{\left[(z - \epsilon_B^s - V_{ss}(E_s(\vec{k}) - \epsilon_B^s)/V_{ss})(z - \epsilon_B^d - V_{dd}(E_s(\vec{k}) - \epsilon_B^s)/V_{ss}) - \gamma_{sd}^2 \right]} \\ &= \mathcal{G}_{ss}(E_s(k), E) \end{aligned} \quad (3.12)$$

where $E_s(\vec{k}) = \epsilon_B^s + V_{ss} S(k)$, V_{ss} = hopping integral corresponding to s band for the crystalline system.

V_{dd} = corresponding to d band for the same

γ_{sd} = hybridisation parameter

$S(k)$ = structure factor corresponding to the crystalline system.

Various Green Functions for the crystalline system :

$$\begin{aligned}
 G_{ss}(E) &= \sum_{\vec{k}} G_{ss}(\vec{k}, E) \\
 &= \int_{-\infty}^{+\infty} \sum_{\vec{k}} G_{ss}(\eta, E) \delta(\eta - E_s(\vec{k})) d\eta \\
 &= \int_{-\infty}^{+\infty} G_{ss}(\eta, E) \rho_s(\eta) d\eta \\
 &= \int_{-\infty}^{+\infty} \frac{\{z - \epsilon_B^d - V_{dd}(\eta - \epsilon_B^s)/V_{ss}\} \rho_s(\eta) d\eta}{[\{z - \epsilon_B^s - V_{ss}(\eta - \epsilon_B^s)/V_{ss}\} \{z - \epsilon_B^d - V_{dd}(\eta - \epsilon_B^s)/V_{ss}\} - \gamma_{sd}^2]} \\
 &\quad z \rightarrow E + i0^+ \\
 &= \int_{-\infty}^{+\infty} \frac{\{z - \epsilon_B^d - V_{dd}(\eta - \epsilon_B^s)/V_{ss}\} \rho_s(\eta) d\eta}{[(z - \eta) \{z - \epsilon_B^d - V_{dd}(\eta - \epsilon_B^s)/V_{ss}\} - \gamma_{sd}^2]} \\
 &\quad z \rightarrow E + i0^+
 \end{aligned}
 \tag{3.13}$$

where $\rho_s(\eta)$ = density of states of s-band for the crystalline system, i.e. the host (B).

Proceeding in the same way, one can have, integral representation also for d-band given by

$$\begin{aligned}
 G_{dd}(E) &= \int_{-\infty}^{+\infty} \frac{\{z - \epsilon_B^s - V_{ss} \frac{(\eta - \epsilon_B^d)}{V_{dd}}\} \rho_d(\eta) d\eta}{[\{z - \epsilon_B^s - V_{ss} \frac{\eta - \epsilon_B^d}{V_{dd}}\} (z - \eta) - \gamma_{sd}^2]} \\
 &\quad z \rightarrow E + i0^+
 \end{aligned}
 \tag{3.14}$$

where $\rho_d(\eta)$ = density of states of d-band in the host similarly integral representation for sd Green Function is given by

$$G_{sd}(E) = \int_{-\infty}^{+\infty} \frac{\gamma_{sd} \rho_s(\eta) d\eta}{[\{z - \epsilon_B^s - V_{ss}(\eta - \epsilon_B^d)/V_{dd}\}(z - \eta) - \gamma_{sd}^2]} \quad (3.15)$$

The relevant representations for disordered alloy Green Functions for various bands in CPA form are the following. Alloy spectral functions are given by,

$$G(k, E) = \begin{pmatrix} E - \Sigma_o^d - V_{dd} S(\vec{k}) & - \Sigma_{sd} \\ - \Sigma_{sd} & E - \Sigma_o^s - V_{ss} S(\vec{k}) \end{pmatrix}^{-1} \quad (3.16)$$

More explicitly,

$$G_{dd}(k, E) = \frac{E - \Sigma_o^s + (V_{ss}/V_{dd})(\epsilon_B^d - E_d(\vec{k}))}{[\{E - \Sigma_o^s + (V_{ss}/V_{dd})(\epsilon_B^d - E_d(\vec{k}))\} \{E - \Sigma_o^d + (\epsilon_B^d - E_d(\vec{k})) - \Sigma_{sd}^2\}]} \quad (3.17)$$

where $E_d(k) = B$ and structure for d-band

$$= \epsilon_B^d + \gamma_{dd}(\vec{k}) .$$

As before,

$$G_{dd}(E) = \int_{-\infty}^{+\infty} \frac{\{E - \Sigma_o^s + (V_{ss}/V_{dd})(\epsilon_B^d - \eta)\} \rho_d(\eta) d\eta}{[\{E - \Sigma_o^s + (V_{ss}/V_{dd})(\epsilon_B^d - \eta)\} \{E - \Sigma_o^d + (\epsilon_B^d - \eta) - \Sigma_{sd}^2\}]} \quad (3.18)$$

Similarly integral representation for s band is given by

$$G_{ss}(E) = \int_{-\infty}^{+\infty} \frac{\{E - \Sigma_o^d - (V_{dd}/V_{ss})(\eta - \epsilon_B^s)\} \rho_s(\eta) d\eta}{[\{E - \Sigma_o^d - (V_{dd}/V_{ss})(\eta - \epsilon_B^s)\} \{E - \Sigma_o^s - (\eta - \epsilon_B^s) - \Sigma_{sd}^2\}]} \quad (3.19)$$

and

$$\bar{G}_{sd}(E) = \int_{-\infty}^{+\infty} \frac{\Sigma_{sd} \cdot \rho_s(\eta) d\eta}{[iE - \Sigma_o^d - (V_{dd}/V_{ss})(\eta - \epsilon_B^s)] \{iE - \Sigma_o^s - (\eta - \epsilon_B^s) - \Sigma_{sd}^2\}} \quad (3.20)$$

We have generated the various Green's Functions in the integral representations by using smoothed version of d-band density of states for Cu through using terminator scheme by C.M.M. Nex in the continued fraction which we have discussed in detail in Chapter 2. Note that since s-band is featureless the standard practice to choose this is of semielliptic form as discussed by Ehrenreich and Schwartz (1976). We have chosen our disordered systems to be the substitutionally random binary alloy $Cu_{1-c}Ni_c$ and selected the various parameters of Cu and Ni from the band structure Table (3.2a) presented by A. Bansil ^{et al.} (1975) for Cu, Ni and the alloy composition, $Cu_{1-c}Ni_c$. If we see the d-band density of states for Cu, we would notice one thing that almost all the structures in the d-band is reproduced except the unusual height of the right most peak. This is due to finite size of the cluster and that we have to compromise so long as we are interested in studying the effect of local environment on the electronic states. The CPA equation for such a system in which s-d hybridisation is a important factor is basically a coupled non-linear equation and this can be solved iteratively starting from guessed solution for

Σ_O^s , Σ_{sd} and Σ_O^d as $(\epsilon_B^s, -i\delta^+)$, $(\epsilon_B^d, -i\delta^+)$, $(\nu_{sd}, -i\delta^+)$ where δ is a small complex part. The governing CPA equation (3.10) together with equations (3.18), (3.19) and (3.20) constitute the working equations to be solved for Σ_O^d , Σ_O^s , Σ_{od} , the three self-energies and hence the three Green Functions $G_{dd}(E)$, $G_{ss}(E)$, $G_{sd}(E)$. So far as the numerical efficiency of solving such equations is concerned, having attained Σ_O^s , Σ_{sd} , Σ_O^d for a given energy E starting with guessed solutions, we use these as the initial iterative values at $E + dE$. At all energy intervals where these self-energies do not change violently, convergence is rapid. At several points convergence may be slow and upto 100 iterations may be necessary.

3.2.2 Results and Discussions on CPA Density of States:

As stated earlier we have generated the d Green Function for the disordered $\text{Cu}_{1-c}\text{Ni}_c$ alloy using the crystalline d-band density of states calculated by Recursion Method for a finite size cluster and ten level of recursion co-efficients (a_n, b_{n+1}) as shown in Table (3.1). Haydock (1980) has discussed the Recursion algorithm in detail for the d-band of a f.c.c. crystal. We have made use of the most recent version of the Recursion Program Library in which the newly developed terminator scheme for Green Function by Haydock and Nex (1984) has been used. The only mismatch is the right most peak in the density of states in the pure case compared to the density of states as shown by Bansil et al (1975). But

TABLE 3.1

CHAIN PARAMETERS FOR d ELECTRONS IN AN FCC CRYSTAL

n	a_n	b_n^2	a_n	b_n^2
Orbital 1		Orbital 4		
0	0.0	0.100000E + 01	0.0	0.100000E + 01
1	-0.736282E - 02	0.295643E - 02	-0.262667E - 02	0.211155E - 02
2	-0.285673E - 01	0.235335E - 02	-0.833132E - 02	0.158428E - 02
3	-0.160718E - 01	0.179840E - 02	-0.962267E - 02	0.121493E - 02
4	-0.134218E - 01	0.162690E - 02	-0.540195E - 02	0.601881E - 03
5	-0.112190E - 01	0.156254E - 02	-0.472927E - 02	0.131840E - 02
6	-0.131124E - 01	0.174530E - 02	-0.398838E - 02	0.869993E - 03
7	-0.671958E - 02	0.153999E - 02	-0.611713E - 02	0.895845E - 03
8	-0.165180E - 01	0.195674E - 02	-0.219311E - 02	0.854633E - 03
9	-0.123618E - 01	0.173710E - 02	-0.107605E - 01	0.126003E - 02
10	0.0	0.168461E - 02	0.0	0.125162E - 02
Orbital 2		Orbital 5		
0	0.0	0.100000E + 01	0.0	0.100000E + 01
1	-0.736282E - 02	0.295643E - 02	-0.262665E - 02	0.211155E - 02
2	-0.285674E - 01	0.235335E - 02	-0.833131E - 02	0.158428E - 02
3	-0.203862E - 01	0.205787E - 02	-0.116066E - 01	0.121205E - 02
4	-0.134712E - 01	0.152931E - 02	-0.128611E - 02	0.610331E - 03
5	0.907024E - 03	0.164361E - 02	-0.736858E - 02	0.135928E - 02
6	-0.596882E - 02	0.155990E - 02	-0.194090E - 02	0.985064E - 03
7	-0.463769E - 02	0.131672E - 02	-0.532768E - 02	0.829151E - 03
8	-0.128520E - 01	0.134450E - 02	0.453185E - 04	0.955998E - 03
9	0.128076E - 02	0.160917E - 02	-0.123153E - 01	0.127546E - 02
10	0.0	0.158227E - 02	0.0	0.147460E - 02
Orbital 3				
0	0.0	0.100000E + 01		
1	-0.736282E - 02	0.295643E - 02		
2	-0.285673E - 01	0.235335E - 02		
3	-0.203862E - 01	0.205787E - 02		
4	-0.134712E - 01	0.152932E - 02		
5	0.907012E - 03	0.164361E - 02		
6	-0.596881E - 02	0.155990E - 02		
7	-0.463773E - 02	0.131672E - 02		
8	-0.128520E - 01	0.134450E - 02		
9	0.128075E - 02	0.160917E - 02		
10	0.0	0.158227E - 02		

rest of the structure is similar. We have repeated the CPA calculation for the hybridized s-d hamiltonian for various concentrations ($c =$, 23%, 40%, 50%) of Ni in Cu host (fig 3.1 a,b,c). We observe as it is expected that the impurity sub-band is featureless in all cases and having almost Lorentzian shapes. As the concentration of Ni increases the two major peaks in density of states of pure Cu start vanishing along with the emergence of featureless impurity band and finally for 50% Ni the impurity band density of states results in two big structureless humps. Note that the vanishing of the peaks in the density of states and the loss of structure in impurity band is due to two reasons (i) artifact of single-site effective medium which tries to smooth out the local fluctuation effects (ii) effect of hybridisation. These results are in qualitative agreement with the old calculations by Stocks et al (1971). The self-energies Σ_o^s , Σ_{sd} , Σ_o^d constitute the basic input for the calculation of the cluster CPA density of states. Our main goal would be to study the cluster effects coming from a pair of atoms coupled statistically. The limitation of single-site CPA is recognised from real system results which constitute the basis for development of the generalisation of CPA and the new results that emerge out of it.

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3.3 Electronic Density of States of $\text{Cu}_{1-c}\text{Ni}_c$ in Cluster CPA

We have already given the introduction of ASF (Augmented Space Formalism) in Chapter 2 and also discussed the appropriate approximation which leads to the self-consistent cluster CPA. At the initial stage ASF had proved to be successful in describing the scattering from clusters for single band model systems in 3-dimension by Kumar et al (1983), V.K. Srivastava (1982). Now, here, we are in a stage to apply it to a real system like $\text{Cu}_{1-c}\text{Ni}_c$ alloy where one can judge the new structure in the impurity band that emerge from statistically coupled sites by making comparison with the CPA results that we have already presented in the previous section of this chapter. We have generated the various diagonal and off-diagonal Green Functions required for solving self-consistent CCPA equations in terms of Recursion Co-efficients suitable for f.c.c. d-band.

The calculation we have pursued is a 2-site cluster CPA based on a general s-d model hamiltonian suitable for describing electronic states in transition noble metal alloys. The general tight binding form of the hamiltonian where s-d hybridisation effect is considered written in equation(3.7) in the previous section. We know that the d-band density of states for pure system has much more fine structures in noble and transition metals compared to s-band and it is also very sensitive to the hybridisation effects as discussed

by Hodges et al (1966). So we give primary importance to the d-band of the constituents Cr and Ni of the disordered binary alloy $\text{Cu}_{1-c}\text{Ni}_c$ with the realistic choice of centers of the two d resonances, i.e. the diagonal disorder of the d-band hamiltonian, off-diagonal disorder due to the variation of the width of the d-bands and by generating appropriate local Green Functions in Recursion Method for the d-band of a f.c.c. crystal. It has been seen as discussed in the previous section that d subband due to Ni impurity in Cu host is featureless in CPA and here we are going to investigate the appearance of structure over the impurity band for various concentrations (10%, 23%, 30%, 40%, 50%) of Ni in $\text{Cu}_{1-c}\text{Ni}_c$ for 2-site cluster CPA calculations.

Here in our calculation of 2-CPA density of states we have treated s-band and hybridisation in the ordinary CPA. While d-band we have treated in 2-CPA. We have already derived the 2-CPA results for a single band model Hamiltonian through equations (2.31a, 2.31b, 2.35 and 2.36) in Chapter 2. Here we write down these main equations using the proper notations for various diagonal and off-diagonal Green Functions with respect to site induces corresponding to d-band. The augmented space graph which describes the scattering from statistically coupled with pair is an octagon as shown in Figure (2.2a,b). In our real calculations of density of states of $\text{Cu}_{1-c}\text{Ni}_c$ one should in fact come across the following self energies $\Sigma_o^s, \Sigma_o^d, \Sigma_o^{sd}, \Sigma_o^{ds}, \Sigma_{1s}, \Sigma_{1d}$. Here

$\Sigma_o^s(z)$ & $\Sigma_o^d(z)$ are diagonal self-energies corresponding to the randomness in the site energy terms for s and d-bands respectively in the hamiltonian in equation(3.7). Along with these we come across the two new off-diagonal self-energies $\Sigma_{1s}(z)$ & $\Sigma_{1d}(z)$ in cluster CPA that properly takes into account the randomness in hopping integrals corresponding to s and d-bands of the same s-d hamiltonian . As stated earlier we are interested in studying the diagonal and off-diagonal self-energies $\Sigma_o^d(z)$ & $\Sigma_{1d}(z)$ in the 2-CPA. The self-energies equations for d-band in 2-CPA has the following form:

$$\Sigma_o^d(z) = \tilde{H}_{oo}^{dd} + \sum_{j \neq o} \sum_{k \neq j} \tilde{h}_{oj}^{dd} \cdot g_{jk}^{dd} [\sigma_o, \sigma_1] \tilde{h}_{k\bullet}^{dd} \quad (3.21a)$$

Here $\Sigma_o^d(z)$ is the self-energy corresponding to the diagonal disorder in the Hamiltonian in equation(3.7) in its d-band term.

We have here, j,k the site indices and

\tilde{H}^{dd} = Host d-band hamiltonian in augmented space
 \tilde{h}^{dd} = Bond hamiltonian which connects the bond (of, 1f) with the rest of the octagon in Figure(2.2a,b) corresponding to d-band.

$g^{dd}(z)$ = Green Function corresponding to the renormalised medium (6x6) obtained by partitioning the (2x2) matrix in the basis |of> and |1f> from the (8x8) octagon, in d-band representation.

$$\Sigma_{1d}(z) = \tilde{H}_{01}^{dd} + \sum_{j \neq 0} \sum_{k \neq 1} \tilde{h}_{0j}^{dd} g_{jk}^{dd} [\sigma_0, \sigma_1] \cdot \tilde{h}_{k1}^{dd} \quad (3.21b)$$

where Σ_{1d} is the self-energy corresponding to the off-diagonal disorder in the hamiltonian for its hopping term corresponding to d-band.

Here,

$\sigma_0(z)$ = Diagonal renormalisation parameter

corresponding to the octagonal decoration

$\sigma_1(z)$ = Off-diagonal renormalisation parameter

corresponding to the same octagonal decoration as discussed below,

and j, k being site indices as before.

The renormalisation of the site and bond (in real space) of the rest of the lattice is carried out by the two renormalisation parameters σ_0 and σ_1 given by the following equations which we have derived in Chapter 2.

$$\sigma_{AA} = \sigma_{EE} = \sigma_0(z) = \Sigma_{1d}^2(z) \sum_{k, m \in N_A} G_{km}^{(2)} \quad (3.22a)$$

$$\sigma_{AE} = \sigma_{EA} = \sigma_1(z) = \Sigma_{1d}^2(z) \sum_{k \in N_A} \sum_{m \in N_E} G_{km}^{(2)} \quad (3.22b)$$

where,

$$H^{(2)} = \Sigma_0^d(z) \sum_i P_i + \Sigma_{1d}(z) \sum_{i, j \neq A, E} T_{ij}$$

and $G^{(2)}$ is the Green Function matrix corresponding to $H^{(2)}$ operator in the site indices k, m .

- N_A = Nearest neighbour of A
 N_E = Nearest neighbour of E
 P = Projection operator
 T = Transfer operator.

The above equations (3.21a, 3.21b, 3.22a and 3.22b) constitute self consistent equations for the self-energies $\Sigma_o^d(z)$ and $\Sigma_{1d}(z)$ corresponding to d-band to be solved for characterising the translationally invariant effective medium in 2-CPA and hence to get the density of states. The appropriate Green Functions for d-band and s-bands with s-d hybridisation in which we have considered for calculational purposes d-band in 2-CPA, s-band and s-d hybridisation in CPA have the following analytic representations.

$$G^{2CP} (k, E) = \begin{bmatrix} E - \Sigma_o^d(z) - \Sigma_{1d}(z) S(\vec{k}) & -\Sigma_{sd} \\ -\Sigma_{sd}(z) & E - \Sigma_o^s(z) - \Sigma_{1s}(z) S(\vec{k}) \end{bmatrix}^{-1} \quad (3.23)$$

$$G_{dd}^{2CP} (k, E) = \frac{\{E - \Sigma_o^s + (\Sigma_{1s}/V_{dd})(\epsilon_B^d - E_d(\vec{k}))\}}{[E - \Sigma_o^s + (\Sigma_{1s}/V_{dd})(\epsilon_B^d - E_d(\vec{k}))][E - \Sigma_o^d - \Sigma_{1d} S(\vec{k})] - \Sigma_{sd}^2}$$

or finally,

$$G_{dd}^{2CP} (E) = \int_{-\infty}^{+\infty} \frac{\{E - \Sigma_o^s + (V_{ss}/V_{dd})(\epsilon_B^d - \eta)\} \rho_d(\eta) d\eta}{[E - \Sigma_o^s + (V_{ss}/V_{dd})(\epsilon_B^d - \eta)] \{E - \Sigma_o^d - \frac{\Sigma_{1d}(\eta - \epsilon_B^d)}{V_{dd}}\} - \Sigma_{sd}^2} \quad (3.24)$$

In the same manner, we have s-band Green Function in 2CPA,

$$G_{ss}^{2CP}(E) = \int_{-\infty}^{+\infty} \frac{\{E - \Sigma_o^d - (\Sigma_{1d}/V_{ss})(\eta - \epsilon_B^s)\} \rho_s(\eta) d\eta}{[\{E - \Sigma_o^d - (\Sigma_{1d}/V_{ss})(\eta - \epsilon_B^s) - E - \Sigma_o^s - (\Sigma_{1s}/V_{ss})(\eta - \epsilon_B^s)\} - \Sigma_{sd}^2]}$$

(3.25)

3.4 Results and Discussion

We have solved the CPA and the CCPA equations for Cu rich CuNi alloys in the concentration range 10%, 23%, 30% 40% and 50% of Ni in Cu. Fig.(3.1-3.4) displays these results. Alloying broadens out most of the sharp features in the Cu d-band density of states, as do s-d hybridisation effects within CPA. With increasing concentration the impurity band grows at the expense of the states at the upper edge of the host band.

Let us discuss the impurity band 10% Ni in Cu, against the Table 3.2b, which gives the eigenvalues of finite clusters of Cu and Ni. At these low concentrations, larger Ni clusters are highly improbable. Within the CPA, details of features of clusters containing more than one Ni atom cannot be accurately resolved. The featureless impurity band of the CPA may be associated with the eigenvalue around $E=0.167$ (row 1 of Table 3.2b) broadened by the immersion of the cluster in the infinite solid. The cluster-CPA begins to resolve features in the impurity band. The two peaks seen in the CCPA may be associated with the eigenvalues around $E=0.145-147$ and $0.189-190$ (rows 2,3 of Table 3.2b) related to the bonding-antibonding levels (X3-X5) in Ni. The terminology arises from the fact that in the tight-binding model the corresponding wave functions combine in the same way as bonding-antibonding wavefunctions in molecules. The small peak around $E=0.06-0.07$ probably arises because of the energy level around those energies in small Ni clusters (rows, 2,3 in Table 3.16).

TABLE 3.2a Complex energies (E_1, E_2) = $E_1 + iE_2$ in rydbergs, at symmetry points in $\text{Cu}_x\text{Ni}_{1-x}$. The energy eigenvalues are based on the potential $V_{\text{II}}^{\text{Cu}}$, except when noted otherwise. The symmetry classification of energy levels is given in the first column, which also indicates whether a given alloy d level is derived from Cu- or Ni-like states. The energy zero is taken to be -0.8341 Ry, which is the muffin-tin zero for pure Cu. $E_{\text{II}}^{\text{Cu(Ni)}} = \frac{1}{3} \text{Re}(3E_{\text{II}}^{\text{Cu(Ni)}} + 2E_{\text{II}}^{\text{Cu(Ni)}})$.

State	Cu	$\text{Cu}_{0.75}\text{Ni}_{0.25}$	$\text{Cu}_{0.75}\text{Ni}_{0.25} (V_{\text{II}}^{\text{Cu}})$	$\text{Cu}_{0.5}\text{Ni}_{0.5}$	$\text{Cu}_{0.25}\text{Ni}_{0.75}$	
Γ_1	0.0161	(0.0194, -0.0)	(0.0194, -0.0)	(0.0226, -0.0)	(0.0260, -0.0)	0.
Cu $\left\{ \begin{array}{l} \Gamma_{25'} \\ \Gamma_{12} \end{array} \right.$	0.3808	(0.3822, -0.0038)	(0.4408, -0.0050)	(0.3833, -0.0077)	(0.3841, -0.0116)	
	0.4510	(0.4287, -0.0087)	(0.4844, -0.0140)	(0.4112, -0.0124)	(0.3968, -0.0144)	
Ni $\left\{ \begin{array}{l} \Gamma_{25'} \\ \Gamma_{12} \end{array} \right.$		(0.5645, -0.0286)	(0.5639, -0.0286)	(0.5652, -0.0191)	(0.5661, -0.0095)	0.
		(0.5920, -0.0239)	(0.5950, -0.0197)	(0.6150, -0.0147)	(0.6349, -0.0070)	0.1
Cu $\left\{ \begin{array}{l} X_1 \\ X_3 \\ X_2 \\ X_5 \end{array} \right.$	0.2178	(0.2364, -0.0003)	(0.2809, -0.0002)	(0.2587, -0.0007)	(0.2884, -0.0014)	
	0.2580	(0.2765, -0.0006)	(0.3290, -0.0005)	(0.2984, -0.0016)	(0.3272, -0.0036)	
	0.4997	(0.4518, -0.0132)	(0.5003, -0.0206)	(0.4236, -0.0150)	(0.4022, -0.0155)	
	0.5165	(0.4581, -0.0148)	(0.5039, -0.0222)	(0.4270, -0.0158)	(0.4037, -0.0158)	
Ni $\left\{ \begin{array}{l} X_1 \\ X_3 \\ X_2 \\ X_5 \end{array} \right.$		(0.5317, -0.0310)	(0.5389, -0.0327)	(0.4969, -0.0247)	(0.4560, -0.0185)	0.3
		(0.5403, -0.0313)	(0.5443, -0.0327)	(0.5131, -0.0245)	(0.4793, -0.0171)	0.4
		(0.6199, -0.0195)	(0.6303, -0.0133)	(0.6560, -0.0123)	(0.6853, -0.0060)	0.7
		(0.6312, -0.0181)	(0.6444, -0.0117)	(0.6710, -0.0116)	(0.7029, -0.0058)	0.7
X_4	0.8372	(0.8369, -0.0)	(0.8369, -0.0)	(0.8366, -0.0)	(0.8363, -0.0)	0.8
Cu $\left\{ \begin{array}{l} L_1^I \\ L_1^I \\ L_2^I \end{array} \right.$	0.2347	(0.2516, -0.0003)	(0.2926, -0.0002)	(0.2721, -0.0009)	(0.2993, -0.0017)	
	0.3739	(0.3780, -0.0035)	(0.4361, -0.0044)	(0.3805, -0.0073)	(0.3827, -0.0113)	
	0.5028	(0.4531, -0.0135)	(0.5010, -0.0209)	(0.4243, -0.0152)	(0.4025, -0.0156)	
Ni $\left\{ \begin{array}{l} L_1^I \\ L_1^I \\ L_2^I \end{array} \right.$		(0.5293, -0.0304)	(0.5374, -0.0324)	(0.4939, -0.0240)	(0.4538, -0.0183)	0.38
		(0.5626, -0.0255)	(0.5621, -0.0291)	(0.5612, -0.0194)	(0.5600, -0.0098)	0.58
		(0.6218, -0.0192)	(0.6327, -0.0130)	(0.6586, -0.0121)	(0.6883, -0.0060)	0.71
L_2^I	0.6193	(0.6187, -0.0)	(0.6187, -0.0)	(0.6181, -0.0)	(0.6174, -0.0)	0.61
L_3^I	1.0018	(1.0381, -0.0025)	(1.0554, -0.0016)	(1.0722, -0.0031)	(1.1045, -0.0021)	1.13
$E_{\text{II}}^{\text{Cu}}$	0.4088	0.4008	0.4582	0.3948	0.3892	
$E_{\text{II}}^{\text{Ni}}$		0.5755	0.5760	0.5881	0.5931	0.60

(after Bansil et al . - 1975)

TABLE 3.2b : Impurity levels found for a finite size cluster formed by putting Cu atoms surrounding Ni atoms (starting from one Ni atom at the centre etc.)

TABLE 3.2b

No of Cu	No of Ni	Eigenvalues (Ryd)
12	1	-0.0083, 0.07, 0.167
11	2	-0.0080, 0.059, 0.145, 0.181
10	3	-0.0080, 0.049, 0.145, 0.147, 0.190
9	4	-0.0080, 0.041, 0.144, 0.147, 0.189
8	5	-0.0083, 0.033, 0.144, 0.147, 0.208
1	1	-0.0031, 0.12

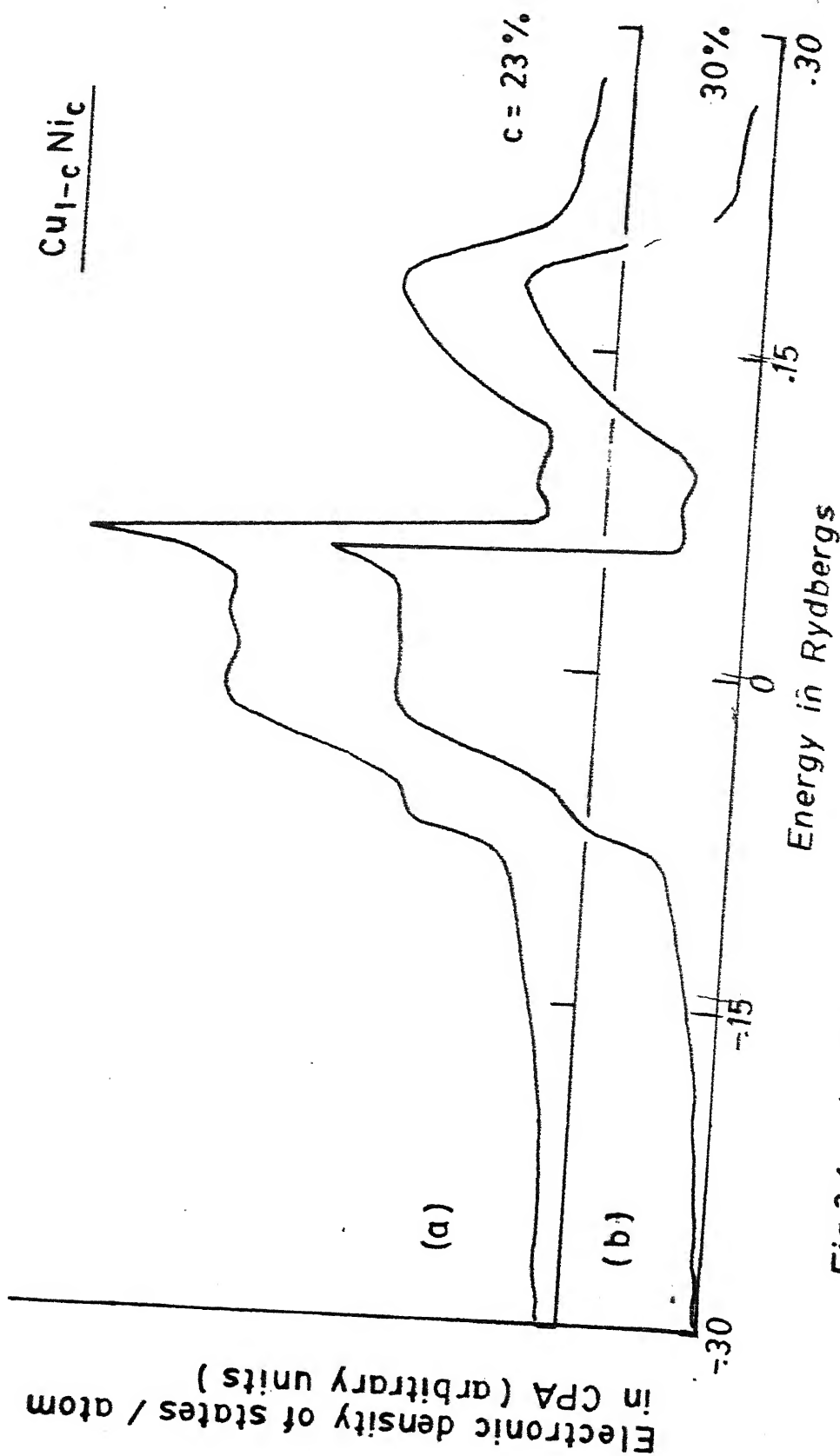


Fig 3.1 a,b Electronic density of states for $c = 23\%$ & 30% Ni in $\text{Cu}_{1-c}\text{Ni}_c$ alloy in single-site CPA

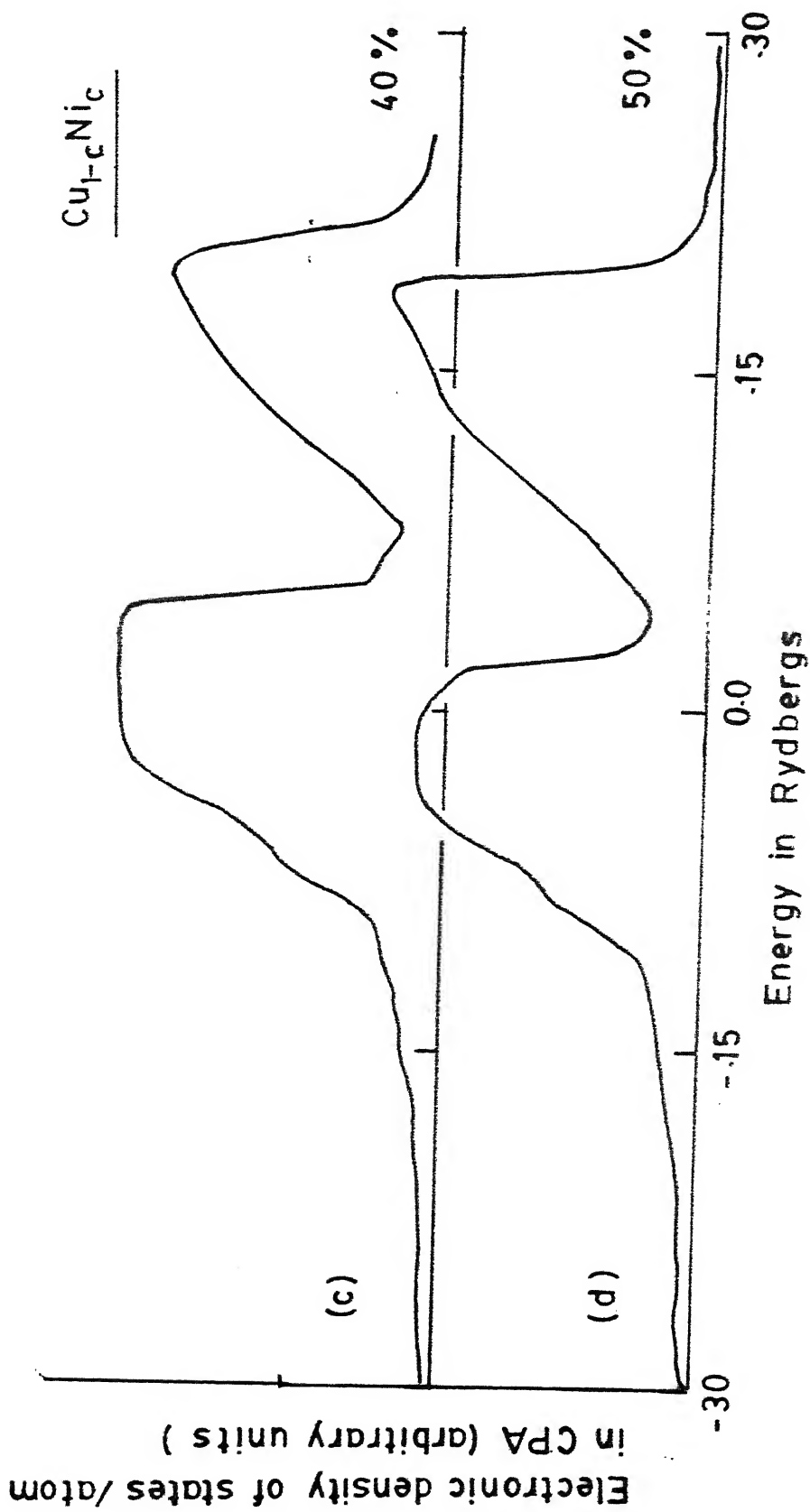


Fig.3.1c, d Electronic densities of states for $c = 40\%$ and 50% .
Ni in $\text{Cu}_{1-c}\text{Ni}_c$ alloy in single-site CPA

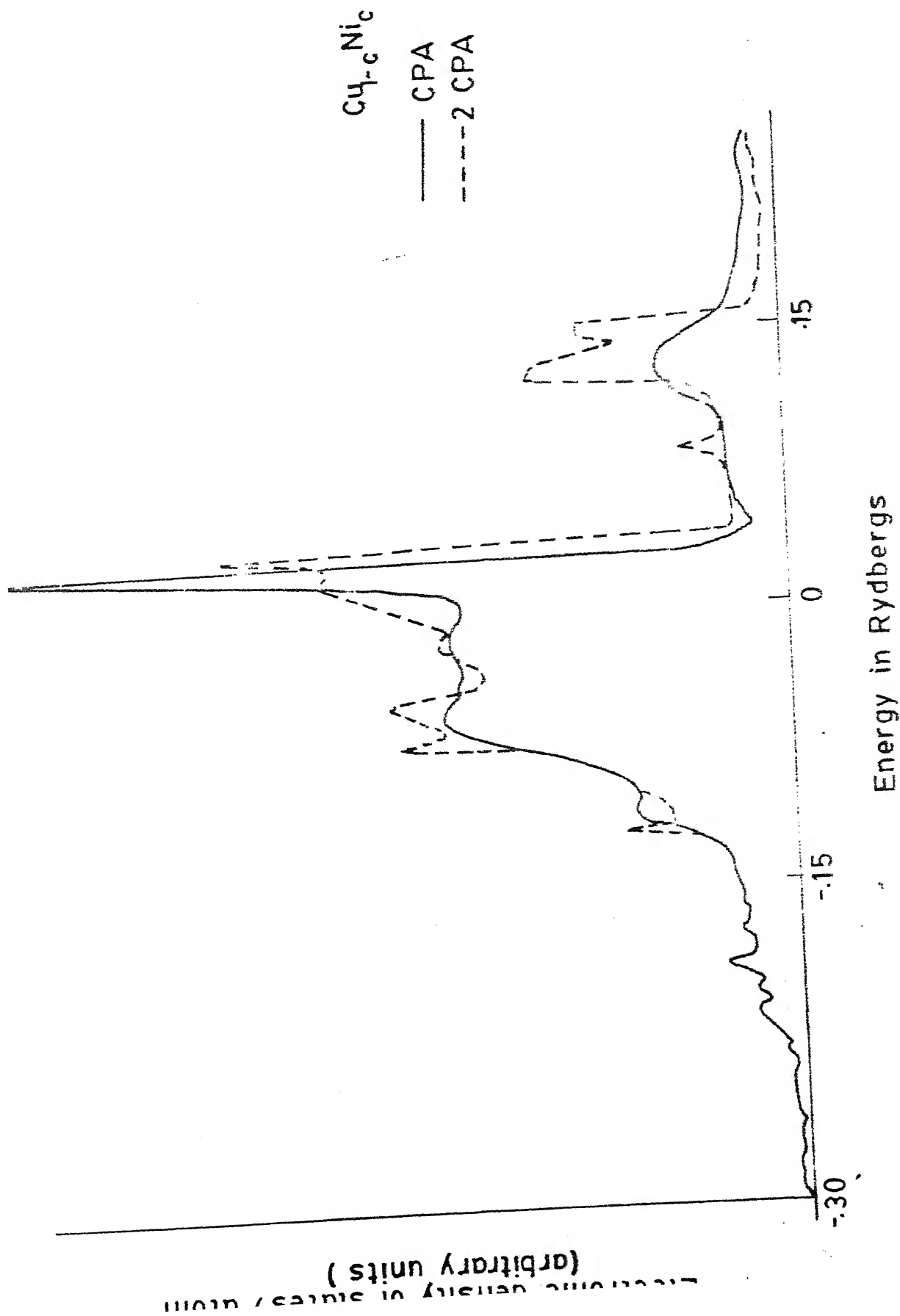


Fig 3.2 Electronic density of states in CPA and 2 CPA
for $\text{Cu}_{1-c}\text{Ni}_c$; $c = 10\% \text{ Ni}$

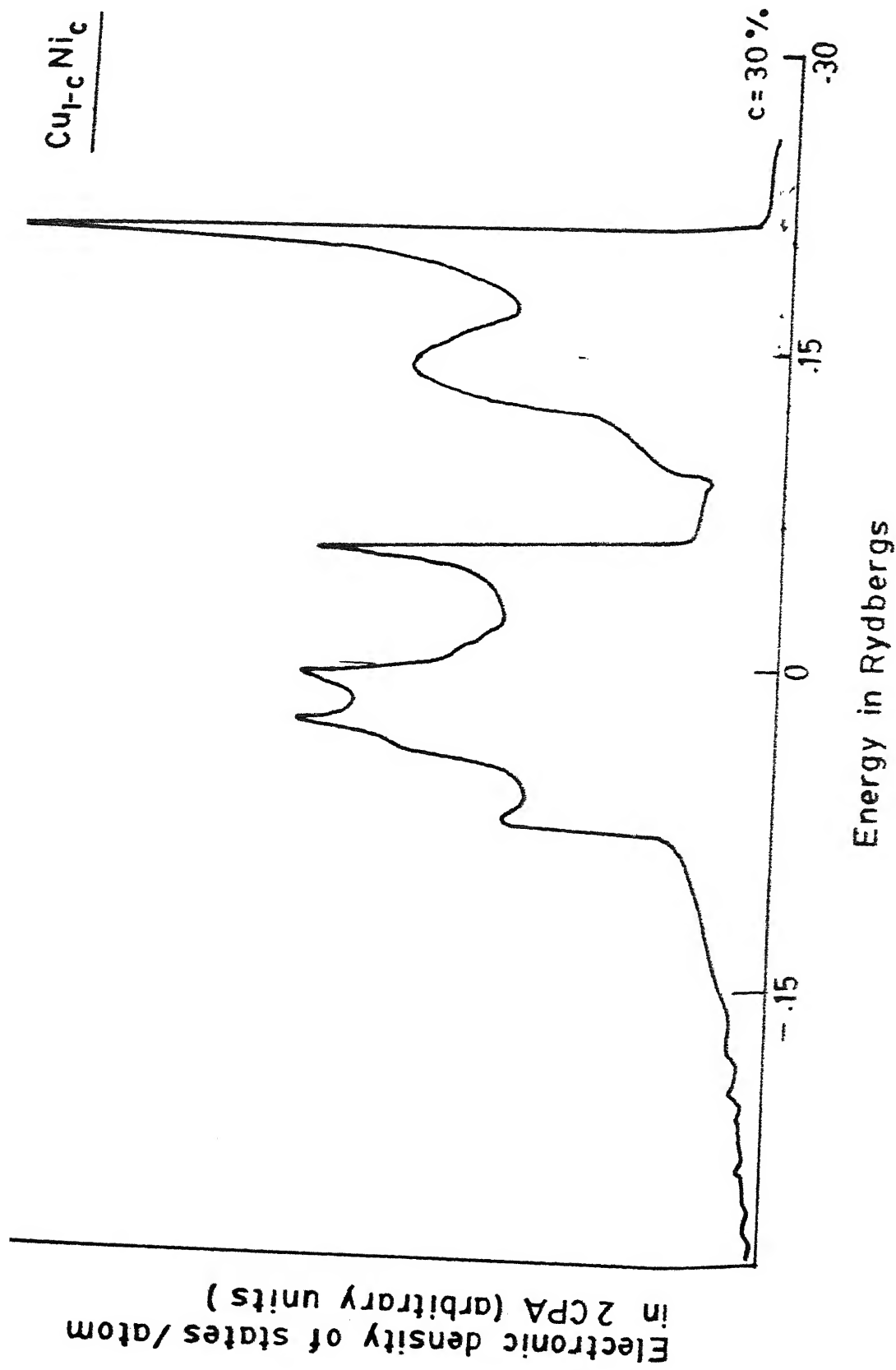


Fig. 3.3 (a) Electronic density of states for $c = 30\%$ in $\text{Cu}_{1-c}\text{Ni}_c$ alloy in 2 CPA

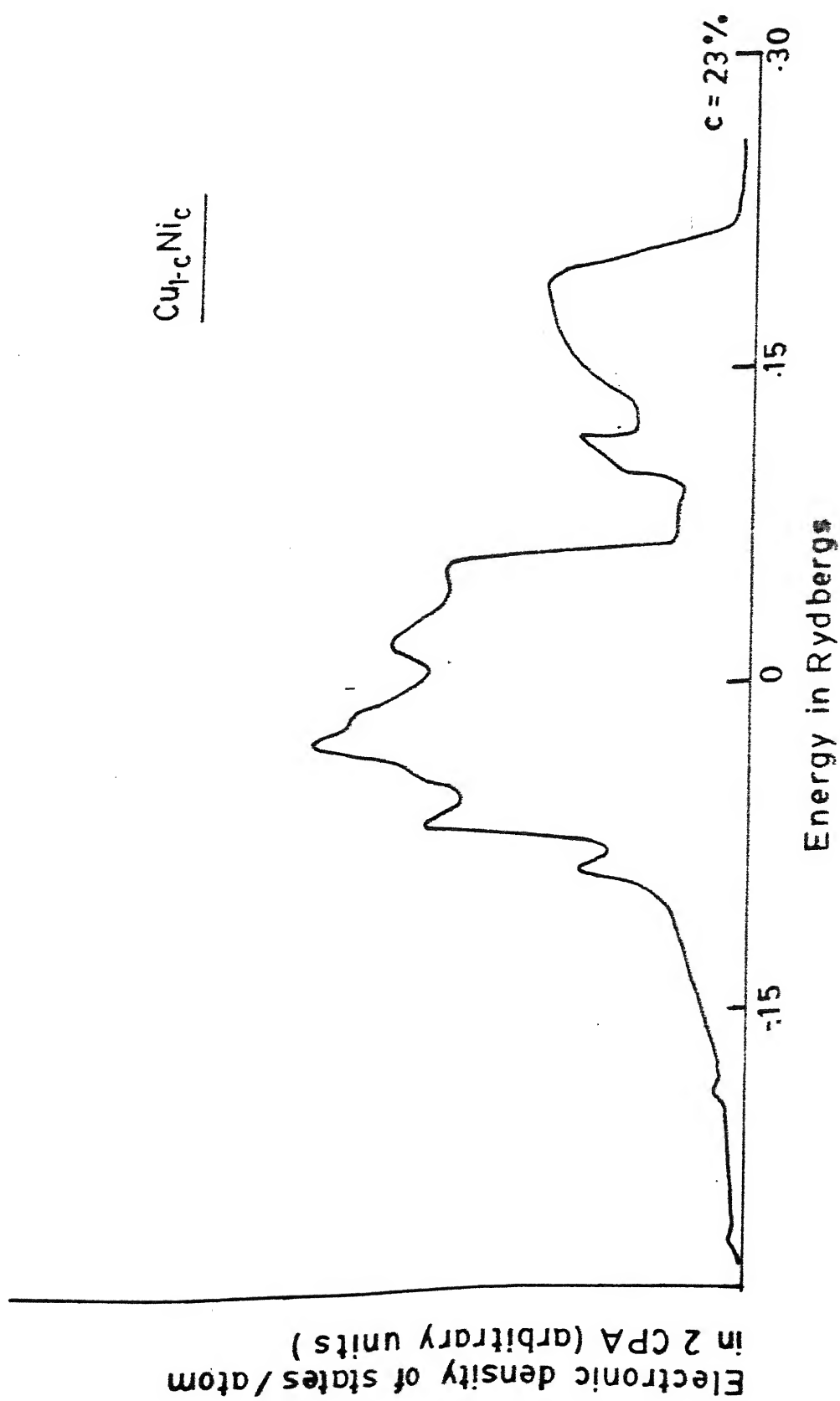


Fig. 3.3 (b) Electronic density of states for $c = 23\%$ Ni in $\text{Cu}_{1-c}\text{Ni}_c$ alloy in 2 CPA

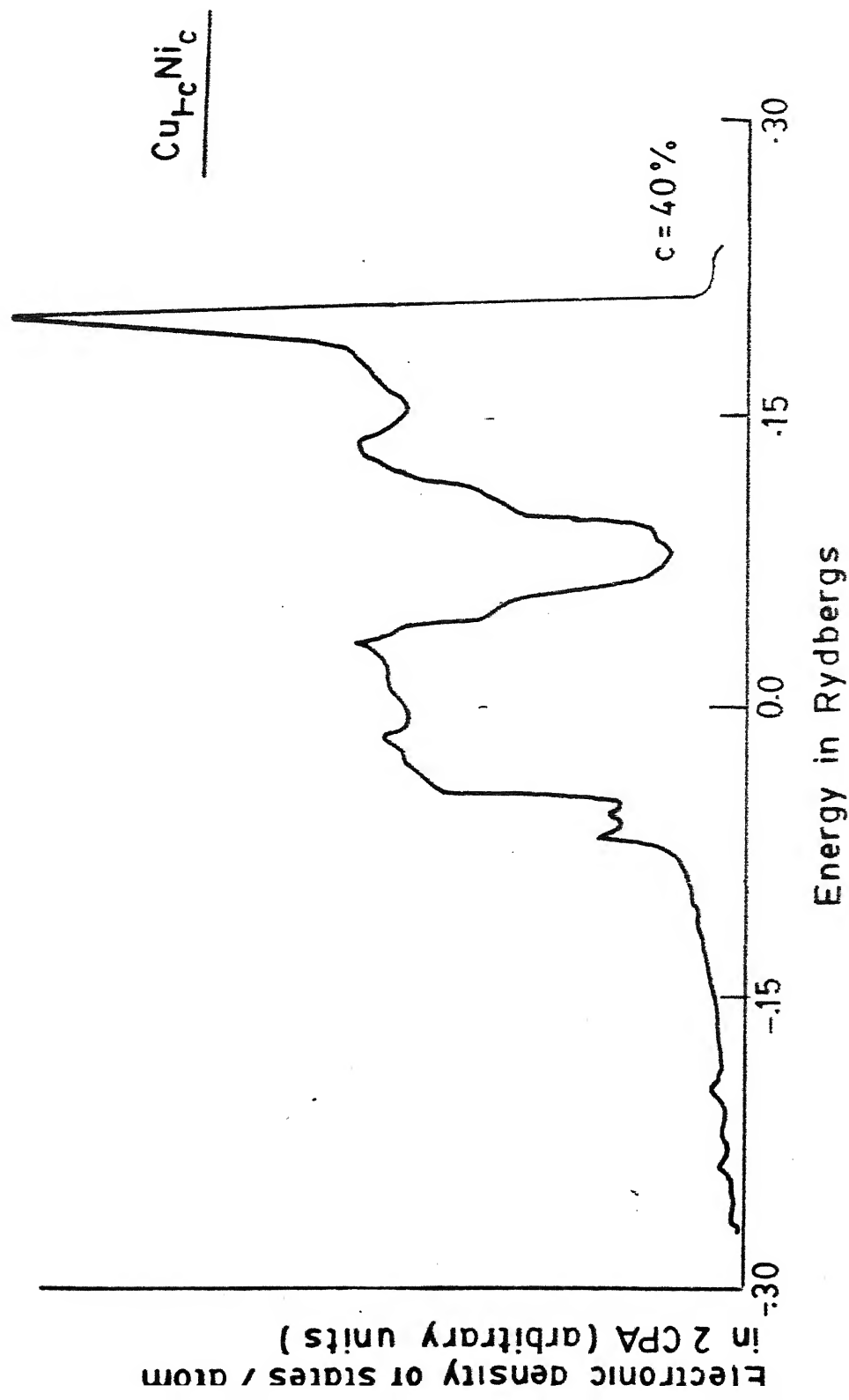


Fig. 3.4 (a) Density of states for $c = 40\%$ Ni in $\text{Cu}_{1-c}\text{Ni}_c$ alloy in 2 CPA

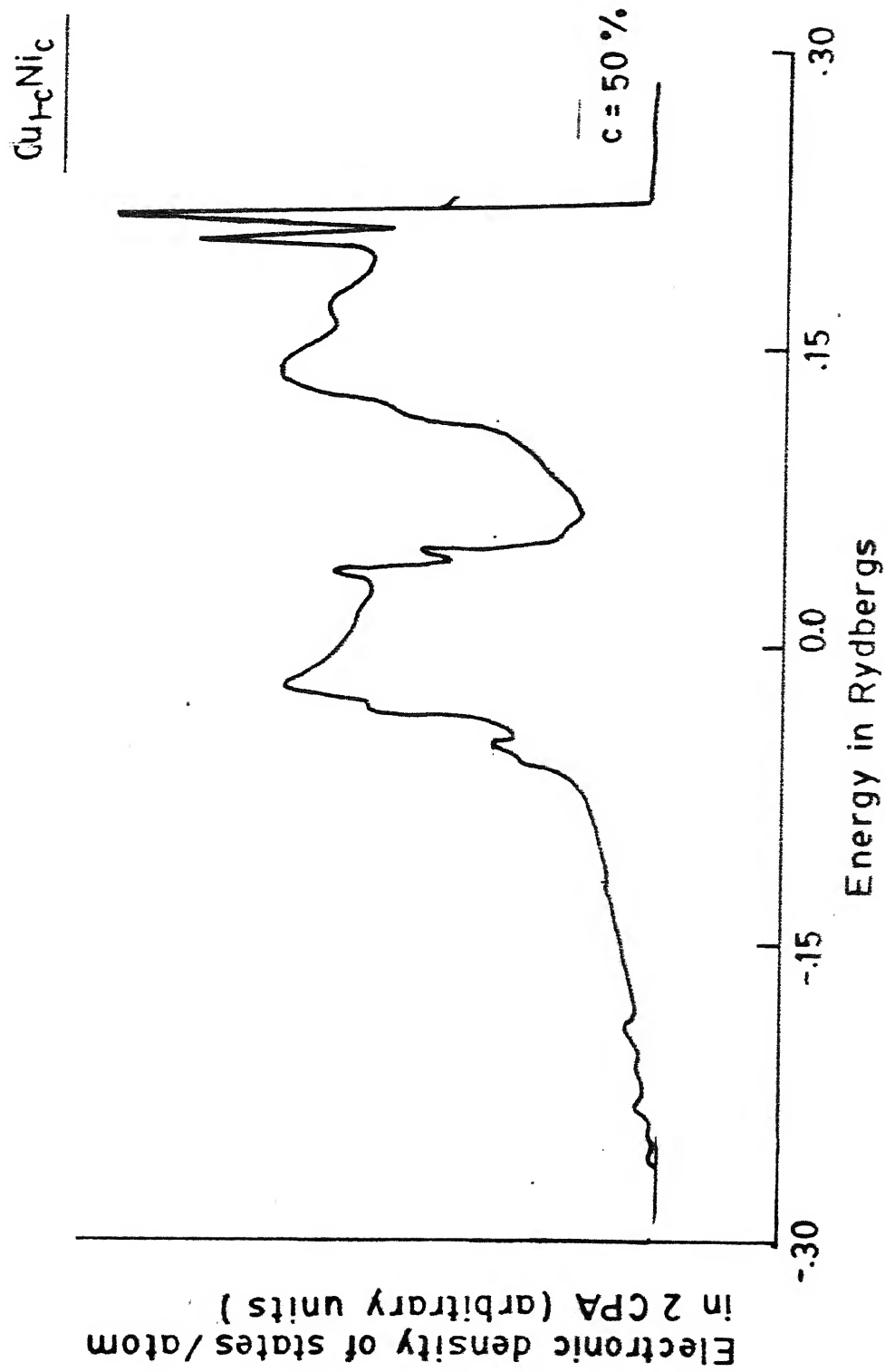


Fig. 3.4 (b) Density of states for $c = 50\%$ Ni in $\text{Cu}_{1-c}\text{Ni}_c$ alloy in 2 CPA

As we go on increasing the Ni concentration, the structure develops strongly around 30% Ni in the impurity band. The structure is reminiscent of the t_{2g} structure in pure Ni and continues to be present upto 50% Ni. We may compare these results with the 13-size cluster calculation by Stocks using the Lloyd formula as reported by Faulkner (1982). They compare very well, except for the exaggeration of the rightmost "antibonding" peak, which in our case is an artifact of the small cluster recursion used (this is clear from the similar exaggeration for pure Cu and Ni). Such structure arising from clusters are not expected to be seen in the CPA.

An alternative approach to the nearly free electron-tight binding (NFE-TB) type formulation we have followed in this work is the KKR-CPA developed for various metallic alloys (Stocks et al 1978; Temmerman et al 1978). The method has been made tractable by the development of fast Brillouin zone integration techniques (Bansil and Prasad 1975). In a review paper on alloys Faulkner (1982) compares the results on various binary alloys (CuNi, AgPd etc.) from the two approaches with experiment. His conclusion is that both methods yield as good a result on density of states.

Gonis et al (1984) have attempted an embedded cluster approach (ECM) for AgPd, in which they embed clusters of different configurations in a KKR-CPA (single site) medium. The medium is not self-consistent with the cluster. Faulkner's comments on the approach is instructive: "the method is

just a cobbled up theory. It is not self-consistent in the sense of the CPA or even the MCPA".

The marriage of the recursion method with the augmented space techniques cut down considerably on computation times. Once the CPA has been generated, at most energies the CCPA requires about five iterations for convergence using multi-variate Newton-Raphson method. This is comparable to most KKR-CPA works reported. However at band edges and where new structure appears in the CCPA often the convergence is very slow requiring as many as fifty to a hundred iterations. Again, this is a common feature of all CPA works.

In connection with CCPA work often the statement has been made that the fine structure revealed in the cluster work is not "seen" in say, photoemission experiments, whereas the simple CPA (occasionally convoluted with a Lorentzian resolution function) seems to give a better fit to experiment. This fine structure was first discovered by Dean (1960, 1972) in computer simulation experiments. It was so startlingly different from the picture known at the time from crude mean field work that initially it was thought to be errors in computation. However, careful analysis identified these structures as arising from resonant scattering from clusters of different sizes and shapes immersed in the infinite matrix. The weight of the peaks are related to the probability of the clusters appearing in a random array, and is therefore strongly influenced by local short ranged order. The CPA being

a single site mean field theory cannot reproduce such fine structure. Similarly experiments (such as photoemission) always have finite resolving power. No optical experiments can measure density of states directly. Usually response involves the density of states convoluted with functions (e.g. transfer matrices, surface and many-body effects) which for disordered systems may have strong energy dependences (Nowak and Dederichs 1985; Mookerjee 1986b). It is not surprising that the CPA, which smoothens out the density of states seems to agree better with experiments, which also measures the density of states smoothed out by different effects (Faulkner 1982). But this does not mean that cluster resonance structure is unimportant. Indeed, the electronic driving force that would cause an order-disorder transition in a crystal has its origin in the resonance structure in the density of states.

3.5 Conclusion

It would be very interesting to note that CCPA in augmented space formalism has been also applied to describe phonon density of states in disordered binary alloys like NiPt (1985), NiPd and NiCr alloys (1982) where the traditional mass CPA failed because of strong clustering and force constant disorders. The underlying physics of cluster induced states in density of states of electron and phonon have close similarities in the sense that wherever the diagonal and off-diagonal disorder or the off-diagonal one is strong one can do calculation in CCPA to describe the density of states within ASF which is an unified approach for random systems.

In conclusion, we have presented a method of obtaining a self-consistent cluster CPA. Here, we have for the first time performed the calculation of electrical density of states in CCPA for realistic disordered metallic alloy like $\text{Cu}_{1-c}\text{Ni}_c$, a canonical system which has received attention both from theoretical and experimental point of view in the past. Our calculation is done in 2-site cluster CPA and resembles the new structures in the density of states which appears to be of very general nature.

This shows how important is the cluster effects at its minimum size and in fact for a system where the disorder is strong one should do CCPA where the size of the cluster

concerned should be of the order of the number of nearest neighbours. Ofcourse, the formalism is valid there but the numerical evaluation of the various self-energies would be very cumbersome.

CHAPTER 4

RESIDUAL CONDUCTIVITY OF RANDOM BINARY ALLOYS IN CPA AND CCPA

4.1 Introductory Remarks on the Development of Residual Conductivity

We have concentrated so far on the electronic density of states in disordered alloys within the co-herent Potential Approximation (CPA) and its generalisation CCPA in which effects of statistically coupled clusters as well as off-diagonal disorder have been treated self-consistently.

Another important physical quantity of interest from theoretical as well as experimental point of view is the residual conductivity describing the electronic states and its transport in disordered metallic alloys in d.c. electric field. Our interest would be to study the conductivity as an energy functional throughout the band in the spirit of CCPA in ASF. The residual conductivity would be the value of this functional at $E = E_f$, the Fermi energy.

We shall first recapitulate the older theories of conductivity based on the CPA in detail with a view to point out the shortcomings like the vanishing of the vertex correction, non-random nature of the current etc., which can lead to significant loss of fine structure in the conductivity results as compared to the CCPA results based on ASF. Such a recapitulation will indicate a way of generalising the older theories so as to overcome the

shortcomings and formulate a method that is feasible and yields physically valid results in realistic systems.

4.2 Various Developmental Stages for the Residual Conductivity in Disordered Alloys:

Theoretical development of conductivity in random alloys has been carried out in several simple situations. The Ziman-Faber theory (Ziman 1961, Bradley 1962, Faber and Ziman 1965) developed originally for liquids but applicable also to alloys, is valid for weak scattering of the conduction electrons by a distribution of dilute random scatterers. The Ziman-Faber theory a nearly free electron picture within the Born approximation is valid only for low concentrations of scatterers, the resulting mean free path is much larger than Debroglie wavelength there. For the case of strong scattering, in transition or noble metal alloys, one may use the extended Ziman theory which replaces the scattering potentials by equivalent t matrices is discussed by Evans et al (1971). Roth and Singh (1982) pointed out that the approach neglects multiple scattering effects.

The principal multiple scattering formalisms are the average T -matrix approximation (ATA) and the CPA, the former being nonself-consistent while the latter incorporates self-consistency. It has been discussed by various authors Ducastelle (1972, 1974), Muller-Hartmann, E. (1973) and Mookerjee (1973) that CPA maintains the Herglotz analytic

properties of the Green Function for all concentrations, energies and scattering strengths. Since CPA deals with single site scattering it does not take into account the back scattering effects which is not small in strongly disordered systems.

The calculation of electrical conductivity for disordered binary alloys in the spirit of CPA was introduced by Velicky et al (1969) starting from Kubo-Greenwood formalism (1957,58). The CPA formulation of conductivity has been also applied to s-d model Hamiltonian for simple model systems having semi elliptic density of states both for s and d-bands. But in both the two cases only diagonal disorder was taken into account. Later Niizeki (1974, 1977) tried to generalise the formulation for both diagonal and off-diagonal disorder but in the spirit of CPA and was able to show that the vertex correction is not zero even in a single band case. Until recently Butler et al (1984) have made calculation of electrical resistivity of $\text{Ag}_{1-c}\text{Pd}_c$ alloys in the spirit of KKR-CPA theory, a CPA theory derived from the multiple scattering methods having many features in common with the KKR (Korringa, Kohn and Rostoker) approach to band theory. The basic KKR-CPA equations were derived by Soven (1970), and later on Shiba (1971) and Gyorffy (1972) put them in convenient forms which are of general use today. The general formulation on electrical conductivity based on the Kubo-Greenwood formalism is also

carried out by Butler (1985) through application in one dimension.

Our (1984 , 1986) aim is to present a general formulation of residual conductivity based on Kubo-Greenwood form of the conductivity expression for three dimensional model systems and a realistic system like $\text{Cu}_{1-c}\text{Ni}_c$ in the spirit of cluster coherent Potential Approximation (CCPA) via the ASF. It has been established that ASF is not only proved to yield analytic results for density of states of disordered alloys but this is also true for the residual conductivity in CCPA of the same.

4.3 Older CPA Theories of Residual Conductivity

4.3.1 Theory of Static Electrical Conductivity for Random Binary Alloys by Velicky

The theory of static electrical conductivity for substitutionally disordered random alloys has been carried out by Velicky (1969) starting from Kubo-Greenwood form of the conductivity expression. It is based on the single-site CPA suitable for a tight binding form of the Hamiltonian as in equation (3.1a) in Chapter 3. The starting point of the conductivity formulation is the Kubo-Greenwood expression (1957, 1958)

$$\langle \sigma^\alpha \rangle^\beta = \frac{2\pi e^2}{m^2 \Omega} \int_{-\infty}^{+\infty} d\eta \left(-\frac{\partial f}{\partial \eta} \right) \text{Tr} \left[\frac{p^\alpha \delta(\eta - H)}{p^\beta \delta(\eta - H)} \right] \quad (4.1)$$

where

- $\langle \rangle$ = Notation used for configuration averaging
 $p^{\alpha, \beta}$ = Component of the linear momentum in a given direction (α or β)
 m = Effective mass of the electron
 Ω = Volume of the unit cell
 $f(\eta, T)$ = Fermi-Dirac distribution at temperature T
 H = Tight binding Hamiltonian of the disordered alloys.

Now,

$$\begin{aligned}
 \langle \vec{k} | p^{\alpha} | \vec{k}' \rangle &= m \left(\frac{\partial}{\partial k^{\alpha}} \right) \epsilon(\vec{k}) \delta_{\vec{k}\vec{k}'} \rightarrow 1 \\
 &= m \vec{v}_{\alpha}(\vec{k}) \delta_{\vec{k}\vec{k}'}
 \end{aligned} \quad (4.2)$$

Now using the operator identity,

$$\begin{aligned}
 \delta(\eta - H) &= (2\pi i)^{-1} [G(\eta) - G(\eta^+)] \\
 \eta^{\pm} &\rightarrow \eta \pm i0^+
 \end{aligned} \quad (4.3)$$

Velicky expressed conductivity expression in a convenient form for calculation in the CPA, in the following manner,

$$\sigma^{\alpha\beta} = \frac{2\pi e^2}{m^2 \Omega} \int d\eta \left(-\frac{\partial f}{\partial \eta} \right) I^{p^{\alpha} p^{\beta}}(\eta^+, \eta^-) \quad (4.4a)$$

$$\begin{aligned}
 \text{with } I^{p^{\alpha} p^{\beta}}(\eta^+, \eta^-) &= (4\pi^2)^{-1} \text{Tr } p^{\alpha} [K(\eta^+, p^{\beta}, \eta^-) + \\
 &\quad K(\eta^-, p^{\beta}, \eta^+) - K(\eta^+, p^{\beta}, \eta^+) - K(\eta^-, p^{\beta}, \eta^-)] \\
 \eta^{\pm} &\rightarrow \eta \pm i0^+
 \end{aligned} \quad (4.4b)$$

where

$$K(z_1, p, z_2) = \langle G(z_1) p G(z_2) \rangle \quad (4.4c)$$

is the vertex function. $G(z_1)$ being the Resolvent corresponding to the random alloy Hamiltonian. We note that the quantity $K(z_1, p, z_2)$ to be averaged is a product of two random operators which can not be factored as $\langle G(z_1) \rangle p \langle G(z_2) \rangle$ in general.

Simplification of the equation (4.4c) in terms of configuration averaged Green Function can be done by the following manner. The standard equation defining T-matrix is

$$G = \bar{G} + \bar{G} T \bar{G} \quad (4.5)$$

where, \bar{G} = configuration averaged resolvent

T = functional of self-energy $\Sigma(E)$

G = unaveraged Green Function.

Averaging equation (4.5) on both sides, $\langle T \rangle = 0$ for the self-consistent $\Sigma(E)$. Now substituting equation (4.5) in the expression for vertex function K in equation (4.4b) we have,

$$\begin{aligned} K &= \langle G p G \rangle \\ &= \bar{G} p \bar{G} + \bar{G} \langle T \bar{G} p \bar{G} T \rangle \bar{G} \\ &= \bar{G} (p + \Gamma) \bar{G} \end{aligned} \quad (4.6a)$$

where vertex correction is defined as,

$$\Gamma = \langle T \bar{G} p \bar{G} T \rangle \quad (4.6b)$$

Velicky was able to express the equation for K involving vertex correction Γ in a convenient form suitable for calculation in CPA and he showed that vertex correction vanishes for a single band Hamiltonian having short ranged potentials in the following way.

The expression for K is written as,

$$K = \bar{G} p \bar{G} + \bar{G} \sum_n |n\rangle \langle n| K |n\rangle \langle n| \bar{G} \quad (4.7a)$$

$$\text{using } \Gamma = \sum_n |n\rangle \langle n| K |n\rangle \langle n| \quad (4.7b)$$

where χ is a function of (z_1, z_2) whose explicit form is shown by Velicky as,

$$\chi(z_1, z_2) = \frac{\langle t_n(z_1) t_n(z_2) \rangle}{[1 + F(z_1) \langle t_n(z_1) t_n(z_2) \rangle F(z_2)]} \quad (4.8a)$$

where, scattering matrix $t_n(z)$

$$t_n(z) = [\epsilon_n - \Sigma(z)] / \{1 - [\epsilon_n - \Sigma(z)] F(z)\} \quad (4.8b)$$

Alloy Green Function $\bar{F}(z)$

$$= \langle n | \bar{G}(z) | n \rangle$$

$$= F^0(z - \Sigma(z)) \quad (4.8c)$$

Here,

ϵ_n = site energy; $\Sigma(z)$ = site diagonal self energy

$F^0(z)$ = Green Function corresponding to the pure system.

Now taking diagonal element of equation (4.7a) with respect to Wannier basis, one can write,

$$\langle m | K | m \rangle = \langle m | \bar{G} p \bar{G} | m \rangle +$$

$$\sum_n [F_{m-n}(z_1) F_{n-m}(z_2)] \langle n | K | n \rangle \quad (4.9a)$$

$$\text{where } F_{m-n}(z_1) = \langle m | \bar{G}(z) | n \rangle$$

$$= \langle m | G^0(z - \Sigma(z)) | n \rangle; \quad G^0(z) = \sum_{\vec{k}} |\vec{k}\rangle [z - \epsilon(\vec{k})]^{-1} \langle \vec{k} |$$

$$(4.9b)$$

Velicky obtained the solution of equation (4.7a) by expressing R.H.S. in a Fourier Transformed form as,

$$\langle m | K | m \rangle = N^{-1} \sum_{\vec{k}} e^{-i\vec{k} \cdot \vec{R}_m} a_{\vec{k}} (1 - A_{\vec{k}})^{-1} \quad (4.10a)$$

$$\text{where } a_{\vec{k}} = \sum_m e^{-i\vec{k} \cdot \vec{R}_m} \langle m | \bar{G} p \bar{G} | m \rangle \quad (4.10b)$$

$$\text{and } A_{\vec{k}} = \sum_m e^{-i\vec{k} \cdot \vec{R}_m} F_m \cdot F_{-m} \quad (4.10c)$$

$$\text{Now, } \langle m | \bar{G} p \bar{G} | m \rangle$$

$$= \frac{1}{N} \sum_{\vec{k}} [z_1 - \Sigma(z_1) - \epsilon(\vec{k})]^{-1} m v^{\alpha}(\vec{k}) \dots\dots\dots$$

$$[z_2 - \Sigma(z_2) - \epsilon(\vec{k})]^{-1} \quad (4.11)$$

By time reversal symmetry,

$$\epsilon(\vec{k}) = \epsilon(-\vec{k}) \text{ and } v^{\alpha}(\vec{k}) = -v^{\alpha}(-\vec{k}) .$$

Therefore, we have, from equation (4.11)

$$\langle m | \bar{G} p \bar{G} | m \rangle = 0 \quad (4.12)$$

Hence, from equations (4.10a, 4.10b) and (4.7b) we have, $= 0$.

The vanishing of the vertex correction is the artifact of single-site CPA theory for short ranged potentials.

Velicky derived the CPA equations for residual conductivity in a very simple form after proving the vanishing of vertex correction in the following manner. The quantity $I^{p^{\alpha} p^{\beta}}$ within the energy integral in equation (4.4a) can be evaluated by simplification of the expression for vertex function K in equation (4.6a). We start with the simplification of the term

$$\begin{aligned} & K(\eta^+, p^{\beta}, \eta^-) \\ &= \bar{G}(\eta^+) p^{\beta} \bar{G}(\eta^-) \\ &= \sum_{\vec{k}} |\vec{k}\rangle [\eta^+ - \epsilon(\vec{k}) - \Sigma(\eta)]^{-1} \langle \vec{k} | \\ & \quad p^{\beta} \sum_{\vec{k}'} |\vec{k}'\rangle [\eta^- - \epsilon(\vec{k}') - \Sigma(\eta^-)]^{-1} \langle \vec{k}' | \\ &= \sum_{\vec{k}} \sum_{\vec{k}'} p^{\beta} \frac{\delta_{\vec{k}\vec{k}'}}{\vec{k}} |\vec{k}\rangle (G^R(\vec{k}, E) + i G^I(\vec{k}, E)) \\ & \quad (G^R(\vec{k}', E) - i G^I(\vec{k}', E)) \langle \vec{k}' | \\ &= \sum_{\vec{k}} |\vec{k}\rangle \{ p^{\beta} [G^{R2}(\vec{k}, E) + G^{I2}(\vec{k}, E)] \} \langle \vec{k} | \quad (4.13a) \end{aligned}$$

where G^R = Real part of spectral function $G(k, E)$,

G^I = Imaginary part of spectral function $\vec{G}(k, E)$ and
 $\eta_{\pm} = E_{\pm} + i0^+$.
 In the same manner,

$$K(\eta^-, p^\beta, \eta^+) = \sum_{\vec{k}} |\vec{k}\rangle \{ p^\beta G^{R^2}(\vec{k}, E) + G^{I^2}(\vec{k}, E) \} \langle \vec{k} | \quad (4.13b)$$

$$K(\eta^+, p^\beta, \eta^+) = \sum_{\vec{k}} |\vec{k}\rangle \{ p^\beta [G^{R^2}(\vec{k}, E) - G^{I^2}(\vec{k}, E)] \} \langle \vec{k} | \quad (4.13c)$$

and $K(\eta^-, p^\beta, \eta^-)$

$$= \sum_{\vec{k}} |\vec{k}\rangle \{ p^\beta [G^{R^2}(\vec{k}, E) - G^{I^2}(\vec{k}, E)] \} \langle \vec{k} | \quad (4.13d)$$

Therefore, finally,

$$\begin{aligned} I^{p^\alpha p^\beta}(\eta, \eta) &= \frac{p^\alpha p^\beta}{4\pi^2} \text{Tr} [\sum |\vec{k}\rangle 4 G^{I^2}(\vec{k}, E) \langle \vec{k} |] \\ &= \frac{p^\alpha p^\beta}{\pi^2} [\sum_n \sum_{\vec{k}} \langle n | \vec{k}\rangle G^{I^2}(\vec{k}, E) \langle \vec{k} | n \rangle] \\ &= \frac{p^\alpha p^\beta}{\pi^2} [\sum_{\vec{k}} G^{I^2}(\vec{k}, E)] \end{aligned} \quad (4.14a)$$

Note that $\langle n | \vec{k}\rangle$ and $\langle \vec{k} | n \rangle$ is simplified by using

$$|\vec{k}\rangle = N^{-1/2} \sum_m e^{i\vec{k} \cdot \vec{R}_m} |m\rangle \quad (4.14b)$$

where $|\vec{k}\rangle =$ Block-ket; $|m\rangle =$ Wannier-ket.

Now, finally the conductivity expression has the following form,

$$\sigma^{\alpha\beta} = \frac{2e^2}{\pi\Omega} \int_{-\infty}^{+\infty} d\eta \left(-\frac{\partial f}{\partial \eta} \right) \sum_{\vec{k}} v^\alpha(\vec{k}) v^\beta(\vec{k}) [\text{Im } G(\vec{k}, \eta^+)]^2 \quad (4.15)$$

Velicky was able to derive the weak scattering and Boltzman limit from the above equation (4.15) in straightforward manner.

4.3.2 Residual Conductivity for a s-d Model Hamiltonian in Single Site CPA by Brouers and Vedyayeb

In the previous article we have discussed how the static electrical conductivity of a single-band model with short ranged random scatterers was shown to be exactly solvable in the CPA. Brouers and Vedyayeb (1972) made an attempt to extend the CPA theory to the calculation of conductivity of a two-band model introduced by Levin and Ehrenreich (1970). ^{Levin et al.(1968), Levin (1970)} / which neglects the widths of the d-levels due to d-d hopping, produces alloy density of states exhibiting hybridisation gaps at the d-levels. The previous theories by Friedel (1962) and Gomes (1966) which takes into account the effect of s-d scattering on the resistivity of transition metal alloys was considered only for dilute alloys.

Brouers and Vedyayeb (1972) were successful for the generalisation which takes into account the width of the d-band (of-course within a semielliptic density of states model) and the effect of s-d hybridisation so that it can be used for the complete range of concentrations. It provides a useful tool for investigating possible deviation from Nordheim $c(1-c)$ law (c being concentration of the impurity) behaviour of the resistivity of transition and noble metal

alloys as well as the influence of s-d hybridisation. On the other hand calculation of conductivity by Brouer & Vedyayev (1972) is able to reproduce the weak scattering limit and dilute concentration limit as derived by Gomes (1966) for transition metal alloys.

Brouers et al tried to calculate the configuration alloy averaged electrical conductivity of a disordered binary $A_c B_{1-c}$ whose Hamiltonian has the form,

$$H^{\text{alloy}} = \sum_{\vec{k}} E_s(\vec{k}) | \vec{k}_s \rangle \langle \vec{k}_s | + \sum_{\substack{n,m \\ m \neq n}} t_{mn}^d | md \rangle \langle nd | \\ + \sum_n \epsilon_n^d | nd \rangle \langle nd | + \sum_k \sum_{BZ} \gamma_{BZ}(\epsilon_n^d) (| \vec{k}_s \rangle \langle nd | e^{i\vec{k} \cdot \vec{R}_m} \\ (4.16a)$$

where,

ϵ_n^d = Site energy corresponding to d-band at the nth lattice position

\vec{R}_m = Lattice coordinate corresponding to mth site

$E_{s,d}(\vec{k})$ = Band-structure corresponding to s-band or d-band

BZ = Brillouin zone and

$$t_{mn}^d = N^{-1} \sum_{\vec{k}} E_d(\vec{k}) e^{i\vec{k} \cdot (\vec{R}_m - \vec{R}_n)} \quad (4.16b)$$

Now, as it is expected conductivity will be a matrix in the $\{ | \vec{k}_s \rangle, | \vec{k}_d \rangle \}$ representation they are obtained the s-s, s-d and dd representation of the conductivity — in the following manner:

$$\sigma = \frac{2e^2}{\pi\Omega} \int d\eta \left(-\frac{\partial f}{\partial \eta}\right) \text{Tr} < \underline{v} \text{Im } \underline{G}(\eta + i0) \underline{v} \text{Im } \underline{G}(\eta + i0) > \quad (4.17)$$

Total conductivity,

$$\sigma_T = \sigma_{ss} + \sigma_{dd} + \sigma_{sd} + \sigma_{ds} \quad (4.18)$$

Note that the operators \underline{v} and \underline{G} of the above equations are (2x2) matrices in the basis of s and d bands. Brouers et al derived the following results for s-s, s-d and d-d components of conductivity

$$\sigma_{ss} = \frac{2 \cdot 2e^2}{\pi\Omega} \int d\eta \left(-\frac{\partial f}{\partial \eta}\right) \sum_{\vec{k}} v_s^2(\vec{k}) [\text{Im } \underline{G}_{ss}(\vec{k}; \eta + i0)]^2 \quad (4.19a)$$

$$\sigma_{dd} = 10 \frac{2e^2}{\pi\Omega} \int d\eta \left(-\frac{\partial f}{\partial \eta}\right) \sum_{\vec{k}} v_d^2(\vec{k}) [\text{Im } \underline{G}_{dd}(\vec{k}, \eta + i0)]^2 \quad (4.19b)$$

$$\sigma_{sd} = \sigma_{ds} = \sqrt{10} \cdot 2 \cdot \frac{2e^2}{\pi c} \int d\eta \left(-\frac{\partial f}{\partial \eta}\right) \sum_{\vec{k}} \vec{v}_s(\vec{k}) \vec{v}_d(\vec{k}) \times [\text{Im } \underline{G}_{sd}(\vec{k}, \eta + i0)]^2 \quad (4.19c)$$

In the present case, the self-energy has to be defined in the representation of d states whereas \underline{G}_k can be written as a (2x2) matrix in the basis $\{|k_s\rangle, |k_d\rangle\}$ as,

$$\bar{G}(\vec{k}; z) = \begin{bmatrix} z - E_s(\vec{k}) & -\gamma \\ -\gamma & z - \epsilon^d(\vec{k}) - \Sigma_o^d \end{bmatrix}^{-1} \quad (4.20a)$$

The three Green Functions, $\bar{G}_{ss}(\vec{k}, z)$, $\bar{G}_{dd}(\vec{k}, z)$ and $\bar{G}_{sd}(\vec{k}, z)$ are as follows:

$$\bar{G}_{ss}(\vec{k}, z) = \{z - E_s(\vec{k}) - \gamma^{-2} [z - \Sigma_o^d - \epsilon^d(\vec{k})]^{-1}\}^{-1} \quad (4.20b)$$

$$\bar{G}_{dd}(\vec{k}, z) = \{z - \Sigma_o^d - \Sigma^d(\vec{k}) - \gamma^{-2} [z - \Sigma_o^s(\vec{k})]^{-1}\}^{-1} \quad (4.20c)$$

and

$$\bar{G}_{sd}(\vec{k}, z) = \gamma^{-1} \{ [z - E_s(\vec{k})] [z - \Sigma_o^d - \epsilon^d(\vec{k}) - \gamma^{-2}] \}^{-1} \quad (4.20d)$$

where, v_s = Drift velocity of electron in the s-band

$$= \frac{\partial E_s(\vec{k})}{\partial \vec{k}} ;$$

$\epsilon^d(\vec{k}) = \alpha \epsilon^s(\vec{k})$ and v_d = Drift velocity of electron in d-band

$$= \frac{\partial \epsilon_d(\vec{k})}{\partial \vec{k}}$$

α = constant proportionality factor.

As in the usual CPA equation one can have the self-consistent condition for d-band

$$\langle t_n^d \rangle = 0 \quad (4.21a)$$

$$\text{with } t_n^d = (\epsilon_n^d - \Sigma_o^d) [1 - (\epsilon_n^d - \Sigma_o^d) \bar{F}_{dd}(z, \Sigma_o^d)]^{-1} \quad (4.21b)$$

The final CPA equation of the self-energy Σ_o^d is,

$$\Sigma_0^d(z) = \bar{\epsilon}_d - (\epsilon_A^d - \Sigma_0^d) \bar{F}_{dd}(z, \Sigma_0^d) (\epsilon_B^d - \Sigma_0^d) \quad (4.22a)$$

$$\text{where } \bar{\epsilon}_d = c\epsilon_A^d + (1-c)\epsilon_B^d \quad (4.22b)$$

$$\text{and, } \bar{F}_{dd}(z, \Sigma_0^d) = \Omega(2\pi)^{-3} \int d^3k \{ z - \Sigma_0^d - \epsilon^d(\vec{k}) - \gamma^2 [z - E_s(\vec{k})]^{-1} \}^{-1} \quad (4.22c)$$

γ = hybridisation factor .

Equation (4.22a) for self-energy $\Sigma_0^d(z)$ is solved iteratively with the choice that in the pure metal both s and d unhybridised bands have the same shape and are related by a scaling factor α . The results of density of states and the position of the Fermi level for various concentrations have been shown in Figure (4.1a,b). The corresponding calculation of conductivity is also shown in Figure (4.1c).

Results and Discussion on the Residual Conductivity Calculation of Brouers et al.

As stated earlier that the effect of hybridisation and the finite width of the d-band is taken into account to overcome limitations of the previous theories by Levin et al (1968,1970); Levin (1970); Levin and Ehrenreich (1971) on static residual conductivity. Although density of states that has been used for d and s-band of the pure system is assumed to be of semi-elliptic form yet the results show up the effect of hybridisation and finite width of the d-band on residual resistivity for noble/transition metal alloys atleast qualitatively. If we focus our attention on resistivity

(ρ) versus concentrations (c) curve in Figure(4.2a,b) one can see the striking deviations from the linear dependence of resistivity versus concentration for small concentrations and from Nordheim's $c(1-c)$ law for higher concentrations. In Figure(4.2a) (resistivity vs. concentration) the region of low concentration is magnified in the upper part of the figure(4.2b) and shows the change of the slope of the resistivity curve, correlated with the minimum in the density of states. The asymmetry of the total curve and the sharp maximum at $c = 75\%$ emphasizes the significant contribution of s-d hybridisation in that concentration range.

Mott (N.F. Mott and H. Jones - 1958) has emphasized that in transition metals and transition metal alloys the resistance is mainly due to scattering process in which an electron makes a transition from the s to the d-band, the probability of such a transition being proportional to the density of states in the d-band. With this picture Mott has explained qualitatively the striking deviation from Nordheim's Rule ($\rho \propto c(1-c)$) exhibiting a Matterhorn type behaviour for rather large concentrations (50 to 70%). In Figure(4.1c) conductivity versus E curve the three contributions to conductivity σ_{ss} , σ_{sd} , σ_{dd} are plotted. Here, one can clearly see a very striking feature that σ_{sd} and σ_{dd} can be larger than σ_{ss} in the majority band regime even for a concentration $c = 15\%$. This shows the strong influence of s-d hybridisation in the conductivity.

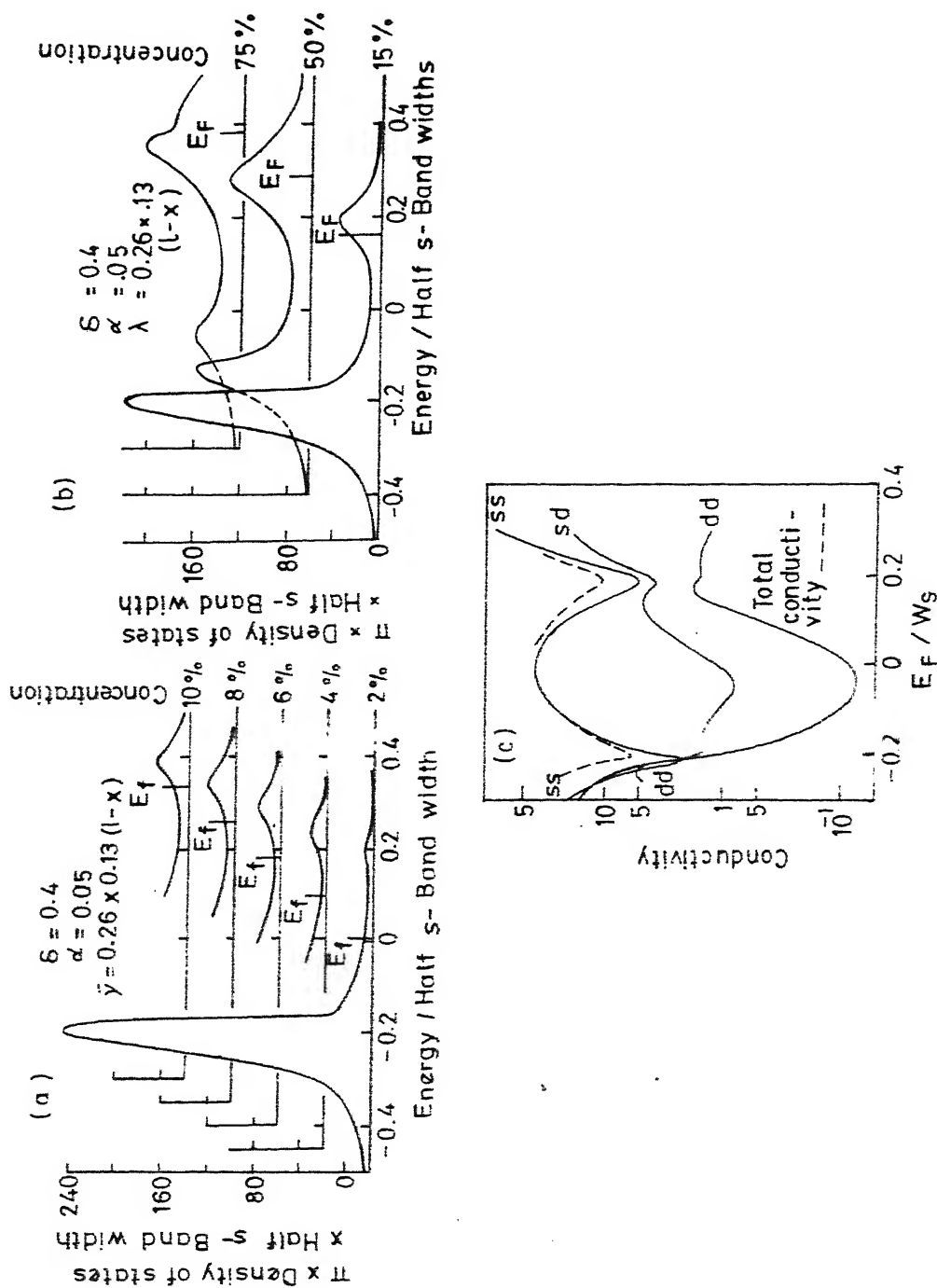


Fig. 4.1 (a & b) The d density of states of the two s-d alloy model for various increasing concentrations
 (c) Total dc electrical conductivity at $T=0$, σ_{ss} , σ_{sd} and σ_{dd} conductivities versus E_F
 (from Brouers and Vedyayev, 1972)

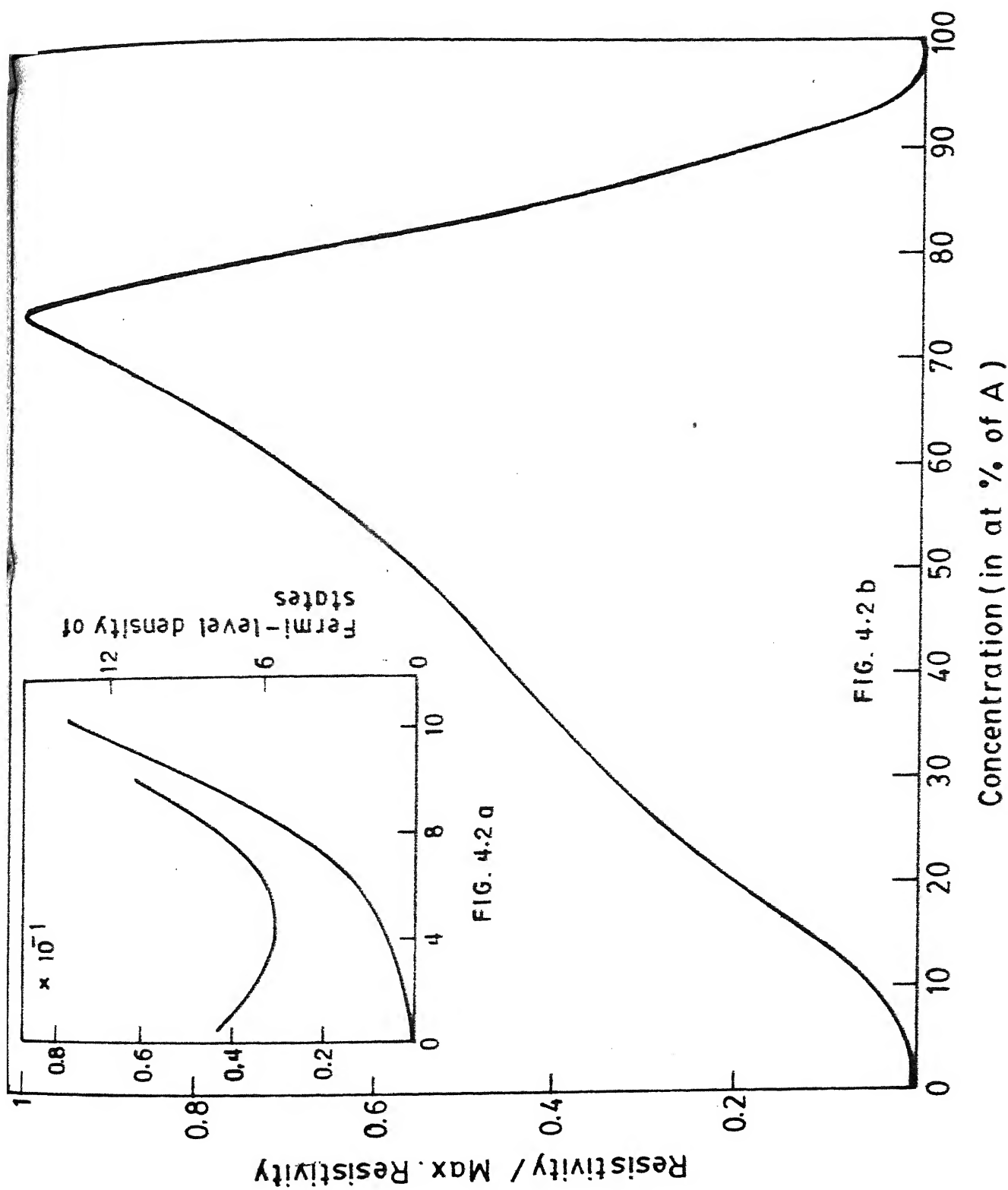


Fig. 4.2 Total residual resistivity versus concentration in units of its maximum value. The asymmetry of the total curve and the sharp maximum at 75% emphasizes the importance of s-d hybridization in that concentration range

The above results that emerge from Brouers & Vedyayev calculation are in agreement with Mott's prediction and experimental results by Nelliset al (1970) which shows an abrupt change in slope of resistivity at about 75% of U in Pd.

4.3.3 Theory of Electrical Conductivity for a Disordered Hamiltonian having both Diagonal and Off-Diagonal Disorder

We have so far discussed conductivity for an Hamiltonian involving diagonal disorder only in single - site CPA. The effect of off-diagonal disorder in a model tight binding Hamiltonian for the electrical conductivity was originally investigated by Niizeki and Endo (1974). They showed that the conductivity is very sensitive to the off-diagonal disorder as well as the diagonal disorder. On the other hand, Fukuyama et al (1974) investigated the case where transfer integrals are additively related. Several authors also tried to generalize further to the case of the model tight-binding Hamiltonian introduced by Blackman et al (1971) when no restriction is imposed on the transfer integrals. A remarkable property of the Hamiltonian is that, in the dilute limit, only the s-like partial waves (those with the complete symmetry of the point group of the lattice) of the scattering due to an isolated, impurity have non-zero scattering amplitudes, and, hence, the total scattering amplitude is isotropic. Consequently, the vertex correction as well as the backward scattering integral in the linearised

where, I_{op} = Unit matrix operator. Green Function corresponding to the random Hamiltonian is given by

$$G(n, z) = (\bar{G}(z) - H(n) + \bar{H}(n, z))^{-1} \quad (4.24b)$$

$$\text{Now, } G(z) = \langle G(n, z) \rangle$$

$$= x G^A(n, z) + y G^B(n, z) \quad (4.24c)$$

where x and y denote respectively concentration of A and B components in the A-B alloy. An alternative form for self-consistency, given by

$$\begin{aligned} & \langle t(n, z) \rangle \\ &= x t^A(n, z) + y t^B(n, z) = 0 \end{aligned} \quad (4.25a)$$

where, $t(n, z)$ is the single-site T-matrix given by,

$$t(n, z) = \{I_{op} - [H(n) - \bar{H}(n, z)] G(z)\}^{-1} [H(n) - \bar{H}(n, z)] \quad (4.25b)$$

The relation between the $t(n, z)$ and the random Green Function $G(n, z)$ is given by,

$$G(n, z) = \bar{G}(z) + \bar{G}(z) t(n, z) \bar{G}(z) \quad (4.25c)$$

Niizeki defined the current operator I and the position operator r_{op} in the following way:

$$r_{op} = \sum_n |n\rangle R_n \langle n| \quad (4.26)$$

$$I = \sum_n I(n), \quad (4.27a)$$

$$\text{where } I(n) = \frac{e}{\hbar} \frac{\partial H(n)}{\partial k} \quad (4.27b)$$

where e = electric charge.

Now, the static electrical conductivity, given by Kubo-Greenwood formula, (1)

$$\sigma_{\alpha\beta} = \frac{2\pi\hbar}{\Omega} \text{Tr} \langle I_{\alpha} (\epsilon I_{op} - H) I_{\beta} \delta(z I_{op} - H) \rangle \quad (4.28a)$$

where, α, β are spatial direction indices, Ω = the volume of the unit cell and z is the energy with an infinitesimal imaginary part 0^+ . Conductivity expression $\sigma_{\alpha\beta}$ can be decomposed into two parts $\sigma^{(1)}$ and $\sigma^{(2)}$ as follows:

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(1)} + \sigma_{\alpha\beta}^{(2)} \quad (4.28b)$$

Here,

$$\sigma_{\alpha\beta}^{(1)} = \frac{\hbar}{\pi\Omega} \text{Tr} \langle I_{\alpha} G_+(z) I_{\beta} G_-(z) \rangle \quad (4.28c)$$

and

$$\sigma_{\alpha\beta}^{(2)} = \frac{-\hbar}{\pi\Omega} \text{Re} \langle \text{Tr} I_{\alpha} G_+(z) I_{\beta} G_+(z) \rangle \quad (4.28d)$$

where $G_{\pm}(z)$ corresponds to Green Functions for $z \pm i0$.

Making use of the identity,

$$G_+(z) I G_+(z) = \frac{e}{\hbar} \frac{\partial}{\partial k} G_+(z) \quad (4.29a)$$

$\sigma_{\alpha\beta}^{(2)}$ can be written as

$$\sigma_{\alpha\beta}^{(2)} = \frac{e^2\hbar}{\pi\Omega} \text{Re} \text{Tr} \langle (m_{op}^{-1})_{\alpha\beta} G_+(z) \rangle \quad (4.29b)$$

where,

$$(m_{op}^{-1})_{\alpha\beta} = \frac{1}{\hbar^2} \frac{\partial^2 H(\vec{k})}{\partial k_\alpha \partial k_\beta} \quad (4.29c)$$

Effective Current Operator: The Vertex Function is defined as,

$$K(z) = G_+(z) I G_-(z) \quad (4.30)$$

Now, Niizeki, introduced an idea of effective (or coherent) current operator $J(z)$ which is periodic and energy dependent but yields the same vertex function as I , i.e.,

$$K(z) = \langle G_+(z) J(z) G_-(z) \rangle \quad (4.31)$$

$$\text{which means } \langle G_+(z) [I - J(z)] G_-(z) \rangle = 0 \quad (4.32)$$

Taking transpose one can also write,

$$\langle G_-(z) [I - \hat{J}(z)] G_+(z) \rangle = 0 \quad (4.33)$$

using $\hat{J}(z) = -J(z)^T$ and inserting the following expressions:

$$\begin{aligned} I &= \hat{J}(z) + [I - \hat{J}(z)] \\ &= J(z) + [I - J(z)]. \end{aligned}$$

Now, the conductivity comes out of the following form,

$$\sigma_{\alpha\beta}^{(1)} = \sigma_{\alpha\beta}^c + \sigma_{\alpha\beta}^{inc} \quad (4.34a)$$

where,

$$\begin{aligned}\sigma_{\alpha\beta}^c &= \frac{\hbar}{\pi\Omega} \text{Tr} [\hat{J}_\alpha(z) \langle G_+(z) J_\beta(z) G_-(z) \rangle] \\ &= \frac{\hbar}{\pi\Omega} \text{Tr} [\hat{J}_\alpha(z) K_\beta(z)]\end{aligned}\quad (4.34b)$$

and

$$\sigma_{\alpha\beta}^{inc} = \frac{\hbar}{\pi\Omega} \langle [\text{Tr}_\alpha \mathbf{I} - J_\alpha(z)] G_+(z) [\mathbf{I}_\beta - J_\beta(z)] G(z) \rangle \quad (4.34c)$$

According to Niizeki (1977) $\sigma_{\alpha\beta}^c$, $\sigma_{\alpha\beta}^{inc}$ are respectively coherent and incoherent parts of the conductivity.

It is important to note that $J(z)$ defined by equations (4.31) and (4.32) can be evaluated easily in the CPA prior to evaluating the vertex function in the following way as discussed by Niizeki and Hoshino (1977).

Neglecting cluster effects on the current term as before in CPA for self-energy, Niizeki introduced the effective single-site current operator. The underlying philosophy remains same and self-consistency is imposed on single site current operator $J(n,z)$ which is the analog of ϵ_n the single-site energy.

We have,

$$J(z) = \sum_n J(n,z) \quad (4.35)$$

The effective single-site current operator $J(n,\epsilon)$ is determined by the condition

$$\langle G_+(n,z) [\mathbf{I}(n) - J(n,z)] G_-(n,z) \rangle = 0 \quad (4.36)$$

using equation (4.32). Now using expression for G from

equation (4.24b) and writing the zeroth site for $J(n, z)$

$$\begin{aligned}
 J(0, z) = & \langle [1_{op} + t_+(0, z) G_+(z)] I(0) \\
 & [1_{op} + G_-(z) t_-(0, z)] \rangle - \langle t_+(0, z) \\
 & G_+(z) J(0, z) G_-(z) t_-(0, z) \rangle
 \end{aligned} \quad (4.37)$$

where $t_{\pm}(0, z)$ is the 0th-site t matrix for energy have been infinitesimal imaginary part $\pm 0^+$. Now, the equation (4.37) provides the evaluation of $J(z)$ in the CPA to the solution of finite system of linear equations for the matrix elements of $J(0, z)$ between the basis vectors.

Evaluation of Vertex Correction

The vertex correction $\Gamma(z)$ in the vertex function $K(z)$ is defined by the equation

$$K(z) = G_+(z) [J(z) + \Gamma(z)] G_-(z) \quad (4.38a)$$

Velicky (1969) has shown that the vertex correction can be divided in the CPA into single-site vertex corrections as

$$\Gamma(z) = \sum_n \Gamma(n, z) \quad (4.38b)$$

Niizeki and Hoshino (1977) showed that the single-site vertex corrections satisfy a coupled set of equations given by

$$\begin{aligned}
 \Gamma(n, z) = & \langle t_+(n, \epsilon) G_+(z) (J(z) + \sum_{n' \neq n} \Gamma(n', z)) \\
 & G_-(z) t_-(n, z) \rangle
 \end{aligned} \quad (4.39a)$$

Equation (4.39a) for the representative site 0 can be written as,

$$\begin{aligned} \Gamma(0,z) &= \langle t_+(0,z) K(z) t_-(0,z) \rangle \\ &\quad - \langle t_+(0,z) G_+(z) \Gamma(0,z) G_-(z) t_-(0,z) \rangle \end{aligned} \quad (4.39b)$$

The above equation gives the representation of vertex-correction in single-site terms. The vertex function and the vertex corrections are determined through introducing an effective current operator $J^*(z)$ different from $J(z)$ by the equation

$$K(z) = G_+(z) J^*(z) G_-(z) \quad (4.40a)$$

Now,

$$J^*(z) = \sum_n J^*(n,z) \quad (4.40b)$$

and

$$J^*(n,z) = J(n,z) + \Gamma(n,z) \quad (4.40c)$$

Now, from equation (4.39a) adding $J(n,z)$ on both sides and after some algebraic manipulation one can get the single-site representation of the effective current operator $J^*(n,z)$.

$J^*(n,z)$ as shown by Niizeki and Hoshino (1977) is given by

$$\begin{aligned}
J^*(n, z) = & \langle [1_{op} + t_+(n, z) G_+(z)] \\
& I(n) [1_{op} + G_-(z) t_-(n, z)] \rangle \\
& + \langle t_+(n, z) G_+(z) \left(\sum_{n' \neq n} J^*(n', z) \right) G_-(z) t_-(n, z) \rangle
\end{aligned}
\tag{4.41}$$

and the vertex function $K(z)$ given by,

$$K(z) = \langle G_+(n, z) [J^*(z) + I(n) J^*(n, z)] G_-(n, z) \rangle
\tag{4.42}$$

Now, equation (4.41) and (4.42) with equation (4.40a,b,c) can be regarded as a self-consistency condition for $J^*(n, z)$.

So, the above mathematical outline shows that in general vertex correction can not be zero in CPA and in fact it can be evaluated in the spirit of effective current approach as stated above. The brief account of numerical results for conductivity calculations done by Niizeki and Hoshino (1977) in a model system is given here.

Numerical Investigation of Static Conductivity by Niizeki and Hoshino

We have previously discussed the theory of electrical conductivity of a random binary alloy which is described by an one electron Hamiltonian in the tight binding approximation with additive randomness. Such type of Hamiltonian can be divided into the unperturbed Hamiltonian describing a periodic reference medium and the scattering potential which can be

divided further into single-site potentials. The main difference between the previous CPA theory of Soven (1967) and the CPA theory used by Niizeki and Hoshino (1977) is that the single-site potentials are long range and nonlocal in general in the latter case. The long range potential may give rise to anisotropy in the differential cross section and since may lead to nonvanishing of the vertex correction.

Previous numerical investigations of the electrical conductivity in the CPA of a random alloy have been carried out only for the case where the scattering potentials are short ranged (Velicky 1969, Levin et al 1970) or the case where the long range can be reduced to the former case by a suitable transformation (Niizeki and Endo 1974; Niizeki and Hoshino, 1975). The vertex correction vanishes in these cases.

Niizeki and Hoshino (1977) calculated numerically the effects of the vertex correction and the nonlocality of the potential on the conductivity.

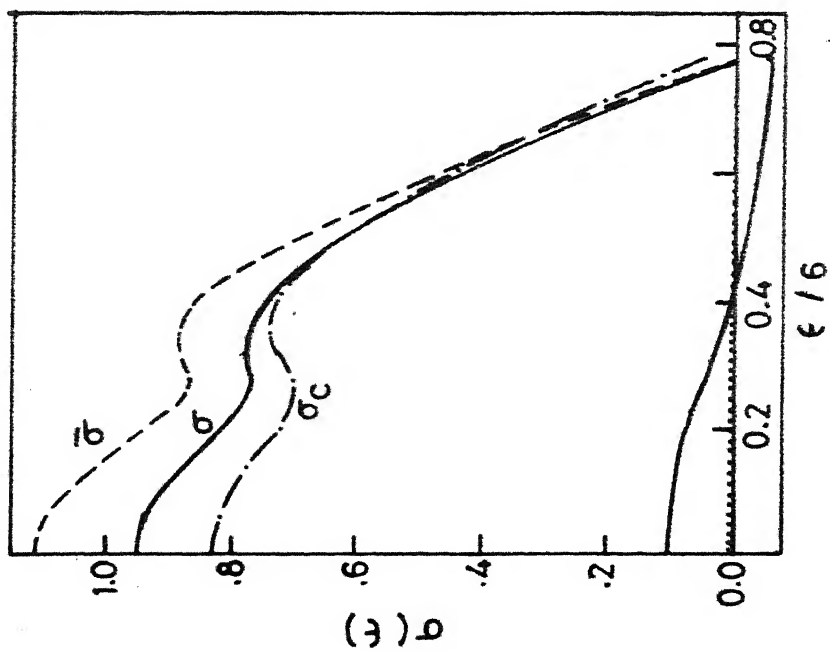
The model they considered is described by a tight binding Hamiltonian given as,

$$H = \sum_{\langle ij \rangle} h_{ij} (|i\rangle \langle j| + |j\rangle \langle i|)$$

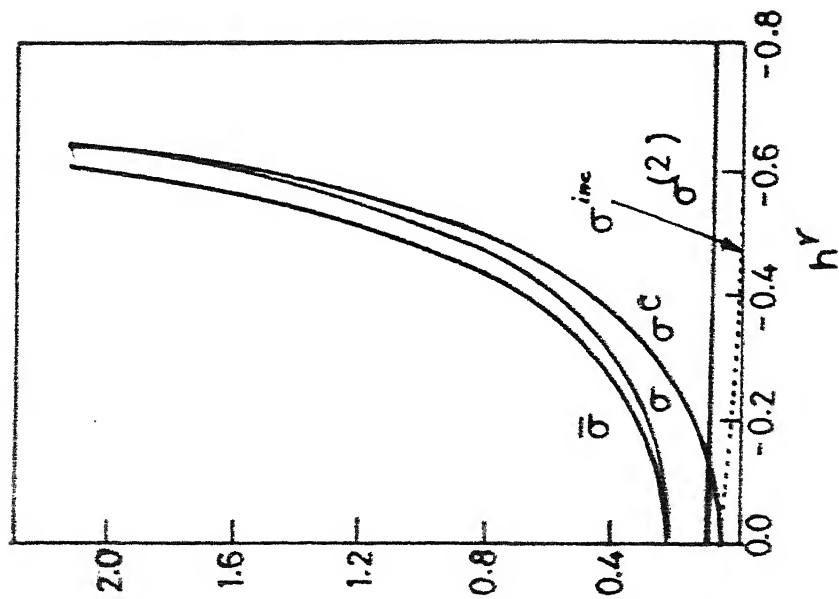
where the summation is limited to nearest neighbour pair of sites in a simple cubic lattice, $|i\rangle$ indicates an atomic orbital of the i th site and h_{ij} is the transfer integral a random variable which takes care of the two possible

negative values h^X and h^Y with possibilities X and Y respectively. This model has only off-diagonal disorder but the character of the off-diagonal disorder is different from that in the Blackman-Esterling-Berk model (1971), Blackman (1975). The present Hamiltonian corresponds to the bond model in the classical percolation problem and the latter one to the site model. Niizeki and Hoshino (1977) computed the density of states and conductivity as an energy functional for $X = Y = 0.5$, $h^X = -1.0$ and $h^Y = -0.5$. Computation of conductivity σ and its three components σ^c , σ^{inc} and σ^2 as energy functional for the above alloy parameters chosen, show very significant effects of vertex correction (as shown in Fig. 4.3a,b).

They also computed the total conductivity $\bar{\sigma}$ without vertex correction. All these results are shown in Figure (4.3a,b). They pointed out from their numerical results that the conductivity is decreased by the vertex correction, because the differential cross-section of the scattering of an electron due to X or Y type bond embedded in the periodic medium in the CPA is larger in the backward scattering (the initial and the final wave vectors k and k' are antiparallel) than the forward scattering (k and k' are parallel). This is evident in the weak-scattering limit when the scattering amplitude is given in the Born approximation is proportional to, say, $\text{Cos } (\vec{k}_x + \vec{k}'_x)a/2$ whose absolute value is larger at $\vec{k} = -\vec{k}'$ than at $\vec{k}' = \vec{k}$.



(a)



(b)

Fig. 4.3

Conductivity σ and its three components, σ^c , σ^{inc} and $\sigma^{(2)}$, as functions of the Fermi level. The conductivities are shown only for $\epsilon \geq 0$ since they are symmetric with respect to ϵ .

Conductivity σ and its three components, σ^c , σ^{inc} and $\sigma^{(2)}$, at the band centre as functions of h^γ for $x=y=0.5$ and $h^x = -1.0$, $\bar{\sigma}^\#$ is the total conductivity without vertex correction.

Drawbacks of the Old CPA Theories on Static Conductivity and the Subsequent Improvements:

In the previous section (4.3) we have given the mathematical outline of the old theories on static conductivity. Drawbacks are the following:

(i) Single-site CPA theory of static conductivity by Velicky proves the vanishing of vertex correction (i.e., the back-scattering effects) for short-ranged potentials of the alloy components. This assumption is not true in general as the potential may be long ranged.

(ii) Brouers & Vedyayeb (1972) generalised the treatment of Velicky for a s-d model Hamiltonian. But they performed the conductivity calculation for a very crude model system where they assumed the s and d bands to have semielliptic electronic density of states. They pointed out only the effect of hybridisation in the residual resistivity results (i.e., the deviation from Nordheim's Rule).

(1977a,b,c)

(iii) Niizeki first proved that the vertex correction in general is not zero in CPA. His calculation was for a model simple cubic lattice. But his conductivity results give a good deal of information about the dependence of conductivity on vertex correction and randomness in current.

4.3.4 Static Electrical Conductivity of Random Binary Alloys in ASF:

Recapitulations of the old theories in electrical conductivity provided us the idea of studying the effect of vertex correction and the randomness in the current on the conductivity for general Hamiltonian where off-diagonal disorder as well as hybridisation should be taken into account. Our aim would be mainly to study the effect of vertex correction and the randomness in current on static conductivity in CCPA via ASF. The effect of off-diagonal disorder and statistical clustering are incorporated through the self-energies corresponding to a finite size of the cluster within CCPA through simplification of the configuration averaged conductivity expression (Kubo-Greenwood form 1957,58).

4.3.5.

An Augmented Space Formalism (ASF) of Electrical Conductivity in Random Alloys within a Cluster Coherent Potential Approximation (CCPA):

The aim of this section is to develop an explicit formalism for calculating the conductivity in the CCPA within the augmented space formalism. We shall illustrate the methodology by application to a simple three-dimensional model alloy first and finally to a realistic system like $\text{Cu}_{1-c}\text{Ni}_c$.

Just as the Herglotz property is essential for any physically meaningful approximation for the one-particle propagator so that the reality of the eigen energies and

positivity and single-valuedness of the density of the states is preserved, Mookerjee (1976) showed that for any approximation for response functions, the vertex correction must be related to the self-energy via a Ward identity, so that averaged macroscopic conservation laws are not violated. Given the self-energy in a CCPA, the Ward identity then provides the vertex correction. This is closely related to the variational procedure of Popeilawski (1979) and that followed by Roth and Singh (1982). The vertex correction with the self-energy is sufficient input for the Bethe-Salpeter equations for the response functions. The Dyson and Bethe-Salpeter equations for the CPA were obtained by laborious diagrammatic resummation by Leath (1970). However, within the augmented space picture, in which k -labelled states are scattered by configuration fluctuations, both were obtained in the CCPA by Mookerjee (1975b,c). These form the background of our present development.

We have already stated that there have been earlier attempts at the theory of conductivity within which off-diagonal disorder was taken into account (Niizeki 1977a,b,c, Hoshino and Watabe 1977, Niizeki and Hoshino 1977). There are several essential differences between the treatment of these and allied works and that of ours (Thakur et al. 1986). All these earlier works were within the framework of the single site CPA, generalising, for long-range potentials, the pioneering work of Velicky (1969). Single-site CPA is

intrinsically unsatisfactory for problems with off-diagonal disorder, where at least the 2 CPA should be considered as the lowest-order approximation. Moreover, except for cases where V_{AB} is either the arithmetic or the geometric average of V_{AA} and V_{BB} , the CPA equations themselves do not simplify. In fact, all CPA work with off-diagonal disorder simply assumes this to be true. As we shall see later in realistic alloys, the presence of short-range order invalidates these assumptions. Within the augmented space approach, no such assumption is necessary (Kumar et al 1982). There is nothing in these works which indicate how to generalise to the CCPA without encountering analytic difficulties. The treatment of the effects due to randomness in the current terms is also different in the two approaches. Finally, all these earlier works envisage only off-diagonal disorder, appropriate to the problem of bond or site percolation; whereas, our approach is applied to a model of an alloy in which there is both diagonal and off-diagonal disorder, statistically coupled. It would be instructive to see how to deal with such a model within the earlier formalisms.

The Mathematics of Static Conductivity Formulation in ASF:

We shall take as our starting point a one-electron, tight binding Hamiltonian with one orbital per site

$$H = \sum_i e_i P_i + \sum_i \sum_j V(r_i - r_j) T_{ij} \quad (4.43)$$

where $P_i = |i\rangle\langle i|$ and $T_{ij} = |i\rangle\langle j|$. The basis functions

are a complete set of linearly independent site labelled functions. In general, orthogonality is unnecessary, although for computational purposes it is convenient. A useful basis are the pseudo-orbitals of the chemical pseudo-potential approach of Bullett (1975), as used by Mookerjee et al (1983). Extension to situations with several orbitals per site is straight forward, involving replacement of scalar quantities like e and V by matrices $[e_{in}]$, $[V_{jm}]$ etc. where n, m label the orbitals. We may go beyond the tight binding and extend our calculations to muffin-tin type of calculations. These extensions will be discussed towards the end of this section.

In a completely random system we have

$$e(r_i) = e_i = e_A n_i + e_B (1 - n_i) = e_B + (e_A - e_B) n_i$$

$$V(r_i - r_j) = V_{AA} n_i n_j + V_{BB} (1 - n_i)(1 - n_j) + V_{AB} \{n_i (1 - n_j) + n_j (1 - n_i)\}$$

$$= V_{BB} + V_1 (n_i + n_j) + V_2 n_i n_j \quad (4.44)$$

where, $V_1 = V_{AA} + V_{BB} - 2V_{AB}$; $V_2 = V_{AB} - V_{BB}$.

Here n_i is a random occupation variable for the site r_i by the species A, with probability.

$$\text{Pr}(n_i) = c\delta(n_i - 1) + (1 - c)\delta(n_i)$$

where c is the concentration of A in B.

Mookerjee (1973) showed that the configuration average of any function of $\{n_i\}$ may be expressed as

$$F(\{n_i\}) = \langle f | \tilde{F}(\{M_i\}) | f \rangle \quad (4.45)$$

where F is the same functional of the operator M_i as F is a function of the n_i . M_i is related to the probability density of n_i . In our case, it is an operator in a vector space φ_i of rank two, whose representation in a basis $\{v_0^i, v_1^i\}$ is

$$M_i = \begin{pmatrix} c & \{c(1-c)\}^{1/2} \\ \{c(1-c)\}^{1/2} & 1-c \end{pmatrix}. \quad (4.46)$$

F is an operator in the space $\Phi = \pi_i \varphi_i$ of rank 2^N and $|f\rangle = \pi_i |v_0^i\rangle$ is the 'reference' configuration, a member in the basis of Φ .

This formalism has been described in great detail in several publications, already referred to, and has been utilised to generate Herglotz, self-consistent CCPA averaged to the single particle propagator $G(r_i, r_j; E)$ via the self-energy matrix (Kumar et al 1982).

The starting point of the conductivity calculations is the Kubo expression

$$\sigma^{\alpha\beta} = \int_{-\infty}^{\infty} dE (-df/dE) \sigma^{\alpha\beta}(E) \quad (4.47)$$

where $f(E)$ is the Fermi function and

$$\begin{aligned} \sigma^{\alpha\beta}(E) &= 2\pi\hbar \text{Tr}\{j^{\alpha\delta} (EI - H) j^{\beta} \delta(EI - H)\} \\ &= (\hbar/\pi) \text{Re} \text{Tr}\{j^{\alpha} G(E^+) j^{\beta} G(E^-) - j^{\alpha} G(E^+) j^{\beta} G(E^+)\} \\ &= \{S^{\alpha\beta}(E^+, E^-) - S^{\alpha\beta}(E^+, E^+)\}. \end{aligned} \quad (4.48)$$

$G(z)$ is the single particle propagator or the Green operator and $j^\alpha = \sum j_{ij}^\alpha T_{ij}$ is the current operator. Like the off-diagonal part of the Hamiltonian, we may write

$$J_{ij}^\alpha(R) = j_{BB}^\alpha(R) + j_1^\alpha(R)(n_i + n_j) + j_2^\alpha(R)n_i n_j$$

with

$$j_1^\alpha(R) = j_{AB}^\alpha(R) - j_{BB}^\alpha(R) ; j_2^\alpha(R) = j_{AA}^\alpha(R) + j_{BB}^\alpha(R) - 2j_{AB}^\alpha(R)$$

and

$$j_\mu^\alpha(R) = (ie/h)R V_\mu^\alpha(R) \text{ or } j_\mu^\alpha(k) = (e/h)\nabla_k^\alpha V_\mu(k).$$

(

In a random system we have to configuration average $\sigma(E)$ and this we shall do within the augmented space formalism. Both the operators G and j are random, involving the random variables $\{n_i\}$. In the earlier attempts by Velicky (1969), and Brouers and Vedyayev (1972), since no off-diagonal disorder was taken into account, randomness in j did not arise. In the work of the Japanese group, randomness in j was accounted for by finding an effective energy dependent current $j(E)$, much in the spirit of the coherent potential itself. The approach of Nowak and Diederichs (1982), in the context of the analogous case of neutron scattering, is also of this nature. Following equation (4.45) we obtain

$$\langle S^{\alpha\beta}(z_1, z_2) \rangle_{av} = (\hbar/\pi) \text{Re Tr} \langle f | j^\alpha \tilde{G}(z_1) j^\beta \tilde{G}(z_2) | f \rangle ; \tilde{G} = (zI - \tilde{H})^{-1}$$

(4.50)

with

$$H = H_B \otimes I + (e_A - e_B) \sum_i P_i \otimes \tilde{M}_i + \sum_{ij} \{V_1 T_{ij} \otimes (\tilde{M}_i + \tilde{M}_j) + V_2 T_{ij} \otimes \tilde{M}_{ij}\} \quad (4.51)$$

and

$$j^\alpha = \sum_{i,j} j_{BB} T_{ij} \otimes I + \sum_{i,j} \{j_1 T_{ij} \otimes (\tilde{M}_i + \tilde{M}_j) + j_2 T_{ij} \otimes \tilde{M}_{ij}\}$$

$$\tilde{M}_i = I \otimes I \otimes \dots \otimes M_i \otimes \dots \otimes$$

$$\tilde{M}_{ij} = I \otimes I \otimes \dots \otimes M_i \otimes \dots \otimes M_j \otimes \dots \otimes I. \quad (4.52)$$

The expressions in (4.52) may be regrouped slightly.

The advantage of such a regrouping would become clear

immediately. If we write $M_i = cP_{vo}i + m_i$, then

$$j^\alpha = \sum_{i,j} \{j_a^\alpha T_{ij} \otimes P_f + j_b^\alpha T_{ij} \otimes (\tilde{m}_i + \tilde{m}_j) + j_c^\alpha T_{ij} \otimes \tilde{m}_{ij}\} \quad (4.53)$$

where

$$j_a^\alpha = c^2 j_{AA}^\alpha + (1-c)^2 j_{BB}^\alpha + 2c(1-c) j_{AB}^\alpha$$

$$j_b^\alpha = c j_{AA}^\alpha + (1-2c) j_{AB}^\alpha - (1-c) j_{BB}^\alpha$$

$$j_c^\alpha = c^2 (j_{AA}^\alpha + j_{BB}^\alpha - 2j_{AB}^\alpha). \quad (4.54)$$

j_a^α is the averaged current, while j_b^α and j_c^α are corrections due to the disorder in the current terms, arising out of off-diagonal disorder. The last of these terms is closely related to the short-range order in the system. If we form an alloy by quenching the melt from a high temperature T_0 , then the configuration which is at equilibrium at T_0 is frozen-in at the lowest temperature. Following Clapp and Moss (1966, 1968), the short-range order parameter,

$$\alpha(R) = \int \frac{d^3k}{8\pi^3} \frac{D e^{-i\vec{k} \cdot \vec{r}}}{1 + 2c(1-c)V_c(k)/k_B T} ; D = \int d^3R \alpha(R) \quad (4.55)$$

and $V_c(R) = V_{AA} + V_{BB} - 2V_{AB}$. Thus unless $V_c(R) = 0$, $\alpha(R) \neq 0$, for $R \neq 0$ and there is always short-range order in the alloy. The Clapp and Moss treatment clearly indicates that in the presence of off-diagonal disorder, unless the alloy is quenched from a temperature much above the critical order/disorder transition temperature where the short-range order vanishes, we must have short-range order characterised by $\alpha(R)$. Our subsequent treatment which includes off-diagonal disorder but ignores short-range order is therefore, not strictly consistent. In any realistic calculation for real alloys we must incorporate short-range order; Kaplan and Gray (1977) have indicated how to do this within the augmented space formalism.

Incorporating the partitioning as in equation (4.54) into (4.50) we obtain nine terms from the cross terms between j_a^α , j_b^α and j_c^α . Consider a few of these:

$$\begin{aligned} S_1^{\alpha\beta}(z_1, z_2) &= (\hbar/\pi) \operatorname{Re} \operatorname{Tr} \langle f | j_a^\alpha G(z_1) j_a^\beta G(z_2) | f \rangle \\ &= (\hbar/\pi) \operatorname{Re} \sum_{i,k,m,n} j_a^\alpha(\vec{r}_i - \vec{r}_k) \langle f | G(\vec{r}_k - \vec{r}_m, z_1) j_a^\beta(\vec{r}_m - \vec{r}_n) \cdot \\ &\quad \cdot G(\vec{r}_n - \vec{r}_i) | f \rangle \\ &= (\hbar/\pi) \operatorname{Re} \int (d^3k/8\pi^3) j_a^\alpha(\vec{k}) L^{\beta(1)}(z_1, z_2; \vec{k}) \end{aligned} \quad (4.56)$$

$$\begin{aligned}
S_2^{\alpha\beta}(z_1, z_2) &= (h/\pi) \operatorname{Re} \operatorname{Tr} \langle f | j_b^\alpha G(z_2) j_a^\beta G(z_2) | f \rangle \\
&= (h/\pi) \operatorname{Re} \sum_{i,k,m,n} [c(1-c)]^{1/2} j_b^\alpha(\vec{r}_i - \vec{r}_k) \\
&\quad \times \langle f_i | G(\vec{r}_k - \vec{r}_m; z_1) j_a^\beta(\vec{r}_m - \vec{r}_n) G(\vec{r}_n - \vec{r}_i; z_2) | f \rangle \\
&= (h/\pi) \operatorname{Re} \int (d^3k/8\pi^3) [c(1-c)]^{1/2} j_b^\alpha(k) L^{\beta(2)}(z_1, z_2; k)
\end{aligned} \tag{4.57}$$

where $|f_i\rangle = |v_1^i\rangle \otimes \pi_{j \neq i}^{\otimes} |v_0^j\rangle$.

$$\begin{aligned}
S_3^{\alpha\beta}(z_1, z_2) &= (h/\pi) \operatorname{Re} \operatorname{Tr} \langle f | j_a^\alpha G(z_1) j_b^\beta G(z_2) | f \rangle \\
&= (h/\pi) \operatorname{Re} \sum_{i,k,m,n} [c(1-c)]^{1/2} j_a^\alpha(\vec{r}_i - \vec{r}_k) \\
&\quad \times \langle f | G(\vec{r}_k - \vec{r}_m; z_1) j_b^\beta(\vec{r}_m - \vec{r}_n) G(\vec{r}_n - \vec{r}_i; z_2) | f_i \rangle \\
&= (h/\pi) \operatorname{Re} \int (d^3k/8\pi^3) [c(1-c)]^{1/2} j_a^\alpha(k) L^{\beta(3)}(z_1, z_2; k).
\end{aligned} \tag{4.58}$$

The first term is the familiar one which arises because of the averaged current $j_a^\alpha(k)$. It is completely diagonal in the augmented space. The next two terms are off-diagonal in augmented space, being taken between the two different configuration bases $|f\rangle$ and $|f_i\rangle$. These nine contributions may be grouped into categories; those diagonal in augmented space and those which are off-diagonal. Let us now examine these contributions in some detail.

The Bethe-Salpeter equation for the two particle propagator

$$G^{II}(\vec{r}_i, \vec{r}_j; \vec{r}_k, \vec{r}_1) = [G(\vec{r}_i, \vec{r}_k)G(\vec{r}_j, \vec{r}_1)]_{av} \quad (4.59)$$

may be schematically expressed as in Figure (4.5a). The equation for $L^{\beta(1)}(z_1, z_2; \vec{k})$ may be obtained by contracting G^{II} with $j_a^\beta(r_j - r_1)$ shown schematically in Figure (4.5b). The resulting Bethe-Salpeter equation may be written as shown:

$$\begin{aligned} L^{\beta(1)}(z_1, z_2; k) &= \bar{G}(z_1; k) j_a^\beta(\vec{k}) \bar{G}(z_2; k) + \bar{G}(z_1; \vec{k}) \bar{G}(z_2; \vec{k}) \\ &\quad \times \int (d^3 k' / 8\pi^3) \Lambda(z_1, z_2; \vec{k}, \vec{k}') L^{\beta(1)}(z_1, z_2; \vec{k}') . \end{aligned} \quad (4.60)$$

This equation provides a self-consistent calculation for $L^{\beta(1)}(z_1, z_2; \vec{k})$ provided the vertex correction $\Lambda(z_1, z_2; \vec{k}, \vec{k}')$ can be found.

The solution to the vertex correction follows from the Ward identity

$$\delta \Sigma(z_1, z_2; \vec{k}) = \int (d^3 k' / 8\pi^3) \Lambda(z_1, z_2; \vec{k}, \vec{k}') \delta G(z_1, z_2; \vec{k}') . \quad (4.61)$$

Let us examine the structure of the vertex correction term in the CCPA scheme in augmented space. Let us focus our attention on the scattering diagrams in augmented space for the vertex correction. These diagrams were discussed in detail in Mookerjee (1975b,c) and we shall take up our analysis from that work.

The single-site CPA involves only those diagrams which include one site (Figure 4.4a), so that the vertex correction is totally diagonal in real space and, because of homogeneity in the augmented space, is k independent. This leads to the vanishing contribution to conductivity, arising out of the antisymmetry of $j_a(\vec{k})$ for reflections, around the origin (Velicky 1969). In the two or any larger cluster CCPA, the vertex term is neither diagonal in real space (Figure 4.4b) nor in k -space. However, inspection of the diagrams reveals an important topological property. Any diagram may be decomposed into two parts (Figure 4.4c) such that either part is any of the diagrams of the series shown in Figure(4.4d). Algebraically this implies

$$\Lambda(z_1, z_2; \vec{k}, \vec{k}') = \lambda(z_1; \vec{k}) \lambda(z_2; \vec{k}') \quad (4.62)$$

The separability of the vertex kernel allows us to solve the integral equation (4.61) explicitly.

$$\Lambda(E^+, E^-; \vec{k}, \vec{k}') = \lambda_1(E^+; \vec{k}) \lambda_1(E^-; \vec{k}') \quad (4.63)$$

$$\Lambda(E^+, E^+; \vec{k}, \vec{k}') = \lambda_2(E^+; \vec{k}) \lambda_2(E^+; \vec{k}') \quad (4.64)$$

$$\lambda_1(E, k) = \frac{\text{Im}\Sigma(E; \vec{k})}{\{ \int (d^3k' / 8\pi^3) [\text{Im} G(\vec{k}', E)] [\text{Im}\Sigma(E, \vec{k}')] \}^{1/2}} \quad (4.65)$$

$$\lambda_2(E, k) = \frac{\Sigma'(E; \vec{k})}{\{ \int (d^3k' / 8\pi^3) \Sigma'(E; k') [\Sigma'(E; \vec{k}') - 1.0] G^2(E; \vec{k}') \}} \quad (4.66)$$

where $\Sigma' =$ Energy derivative of $\Sigma(E; \vec{k})$

Let us concentrate on a two-site CCPA; the Bethe-Salpeter equation (4.60) may be rewritten as shown in Figure (4.5c). On the right-hand side are three types of contributions:

(1) The first term is of zeroth order and its contribution in \vec{k} -space may be written as

$$G(z_1; \vec{k}) j_a^\beta(\vec{k}) G(z_2; \vec{k}) = A(z_1, z_2; \vec{k}) j_a^\beta(\vec{k}) \quad (4.67)$$

(2) The second term arises out of single-site scattering. Note that in the single-site CPA, this is the only vertex correction term that remains. In the 2CPA too, this term must be taken into account. Note, that its contribution in the 2CPA is not identical to that in the 1CPA, since all the internal propagators are $\tilde{G}(z, k)$ calculated within the 2CPA and not the 1CPA. However, the structure of the terms is the same in any CP approximation. The vertex is totally diagonal in real space and independent of k . Its contribution is

$$\Lambda_0 A(z_1, z_2; \vec{k}) \int L^{\beta(1)}(z_1, z_2; \vec{k}) (d^3 k' / 8\pi^3) \quad (4.68)$$

(3) Finally there are the terms arising out of two-site scattering. These are the lowest-order terms of the so-called 'maximally crossed' diagrams. These terms are totally absent in the single-site CPA with short-range potentials. The contribution of these terms in real space is given by:

$$\sum_{s,s'} G(z_1; \vec{r}_i - \vec{r}_s) G(z_2; \vec{r}_{s'} - \vec{r}_j) A(z_1, z_2; \vec{r}_s - \vec{r}_{s'}, \vec{r}_{s'} - \vec{r}_s) L^{\beta(1)}(z_1, z_2; \vec{r}_{s'} - \vec{r}_s) \quad (4.69)$$

Taking the Fourier transform, we obtain the contribution in k -space,

$$A(z_1, z_2; k) \iint \frac{d^3 k'}{8\pi^3} \frac{d^3 k''}{8\pi^3} \lambda(z_1; \vec{k} + \vec{k}' - \vec{k}'') \lambda(z_2; \vec{k}'') L^{\beta(1)}(z_1, z_2; \vec{k}') \quad (4.70)$$

If we look at equation (4.63-4.66), we note that $\Sigma(z; k) = \Sigma_0 + \Sigma_1 s(k)$ where $s(k) = \sum_x \exp(ik \cdot x)$ summed over the nearest-neighbour vectors x on the lattice. The vertex terms arising out of these diagrams contain a part which is k independent (arising out of Σ_0) and a part that does depend on k . We shall absorb the k -independent term with the second term (as it has the same structure). The remaining vertex correction term thus arises essentially from the off-diagonal part of the self-energy. Thus,

$$S_1^{\alpha\beta}(z_1, z_2) = \iint \frac{d^3 k}{8\pi^3} j_a^\alpha(\vec{k}) j_a^\beta(\vec{k}) A(z_1, z_2; \vec{k}) + \iint \frac{d^3 k d^3 k' d^3 k''}{(8\pi^3)^3} j_a^\alpha(\vec{k}) A(z_1, z_2; \vec{k}) \lambda(z_1; \vec{k} + \vec{k}' - \vec{k}'') \lambda(z_2; \vec{k}'') L^{\beta(1)}(z_1, z_2; \vec{k}') \quad (4.71)$$

Equations (4.60)-(4.71) provide us with the basis for obtaining the conductivity, arising out of the averaged current.

$$\begin{aligned}
\delta \Sigma_{\mu\nu}(z_1, z_2; \vec{k}) &= \int \frac{d^3 k'}{8\pi^3} \mu' \nu' \Lambda_{\mu\nu, \mu' \nu'}(z_1, z_2; \vec{k}, \vec{k}') \delta G_{\mu' \nu'}(z_1, z_2; \vec{k}') \\
L_{\mu\nu}^{\beta(1)}(z_1, z_2; \vec{k}) &= \sum_{\alpha, \eta} j_{\alpha\eta}(\vec{k}) A_{\mu\eta, \alpha\nu}(z_1, z_2; \vec{k}) + \sum_{\eta\alpha} \sum_{\sigma\delta} A_{\mu\eta, \alpha\nu}(z_1, z_2; \vec{k}) \\
&\quad \int \frac{d^3 k'}{8\pi^3} \Lambda_{\eta\sigma, \alpha\delta}(z_1, z_2; \vec{k}, \vec{k}') L_{\delta\alpha}^{\beta(1)}(z_1, z_2; \vec{k}') .
\end{aligned}
\tag{4.72}$$

For computational purposes, we may project the matrices on to vectors and supermatrices into matrices. Take, for example, a case with two orbitals per site. Then the 2x2 matrices of the kind $\delta G_{\mu\nu}$ may be written as the 4-vector

$$\delta g_p = (\delta G_{11}, \delta G_{12}, \delta G_{21}, \delta G_{22})^T \tag{4.73}$$

while supermatrices like $\Lambda_{\mu\nu, \alpha\delta}$ may be written as

$$A_{pq} = \begin{bmatrix} \Lambda_{11,11} & \Lambda_{11,12} & \Lambda_{11,21} & \Lambda_{11,22} \\ \Lambda_{12,11} & \Lambda_{12,12} & \Lambda_{12,21} & \Lambda_{12,22} \\ \Lambda_{21,11} & \Lambda_{21,12} & \Lambda_{21,21} & \Lambda_{21,22} \\ \Lambda_{22,11} & \Lambda_{22,12} & \Lambda_{22,21} & \Lambda_{22,22} \end{bmatrix} \tag{4.74}$$

Equations (4.60) and (4.61) may now be rewritten as

$$\begin{aligned}
L^{\beta(1)}(z_1, z_2; \vec{k}) &= L_p^{\beta(1)}(z_1, z_2; \vec{k}) + \sum_{qr} A_{pq}(z_1, z_2; \vec{k}) \\
&\quad \times \int (d^3 k' / 8\pi^3) A_{qr}(z_1, z_2; \vec{k}, \vec{k}') L_r^{\beta(1)}(z_1, z_2; \vec{k}')
\end{aligned}
\tag{4.75}$$

and

$$\delta s_p(z_1, z_2; \vec{k}) = \sum_q \int (d^3 k' / 8\pi^3) A_p(z_1, z_2; \vec{k}, \vec{k}') \delta g_q(z_1, z_2; \vec{k}') \quad (4.76)$$

Equations (4.75) and (4.76) now form the basis of our conductivity calculations.

The Weak Scattering Limit:

Before we contemplate application of our formalism to any system, let us examine the weak scattering limit and compare our results with the well known results which already exist in this regime.

Let us first express the current $j_a(k)$ as $j(k) \cos \varphi(\vec{k}, \vec{r})$ where $j(k)$ is $e\partial E(k)/\partial k$ and $\varphi(\vec{k}, \vec{r})$ is the angle between the direction of \vec{k} and a unit vector in the direction of \vec{r} . Moreover, we shall write

$$L^{\beta(1)}(z_1, z_2; \vec{k}) = j_a^\beta(k) A(z_1, z_2; \vec{k}) W(z_1, z_2; \vec{k}) \quad (4.77)$$

so that the Bethe-Salpeter equation becomes

$$W(z_1, z_2; \vec{k}) = 1 + \int (d^3 k' / 8\pi^3) A(z_1, z_2; \vec{k}, \vec{k}') A(z_1, z_2; \vec{k}') (j(\vec{k}') / j(\vec{k})) \\ \times \cos \varphi(\vec{k}, \vec{k}') W(\vec{k}', z_1, z_2) \quad (4.78)$$

For $z_1 = E^+$, $z_2 = E^-$ we may identify $\delta \Sigma(E^+, E^-; \vec{k}) = -2\text{Im}\Sigma(E, \vec{k}) = \tau_0^{-1}(\vec{k})^{-1}$ an isotropic life time. From the Ward Identity we get

$$\tau_0^{-1}(\vec{k}) = -2 \int (d^3 k' / 8\pi^3) A(E^+, E^-; \vec{k}, \vec{k}') \text{Im}G(E, \vec{k}') \quad (4.79)$$

Noting that

$$G(E^+, \vec{k})G(E^-; \vec{k}) = -2\tau_0^{-1}(\vec{k}) \text{Im}G(E; \vec{k}) \quad (4.80)$$

and in the weak scattering limit the self-energies are small, so that $\text{Im} G(E, \vec{k})$ is strongly peaked around the energy shell $E = E(\vec{k})$. The dominant contribution to the integral on the left-hand side of equation (4.78) then comes from this energy shell. Using these approximations we get $W(E^+, E^-; \vec{k}) = \tau(\vec{k})/\tau_0(\vec{k})$ where we identify a diffusion life time

$$\tau^{-1}(\vec{k}) = -2 \int (d^3 k' / 8\pi^3) \Lambda(E^+, E^-; \vec{k}, \vec{k}') \text{Im}G(E, \vec{k}') [1 - \cos(\vec{k}, \vec{k}')]. \quad (4.81)$$

This is the Rubio result that reduces to the Ziman formula (Rubio 1969).

Turning to the Kubo formula, if we neglect the corrections due to randomness in the current (which is small in the regime under consideration)

$$\sigma^{xx}(E) = (e^2/\pi) \int \frac{d^3 k}{8\pi^3} j^x(\vec{k}) [j^x(\vec{k}) |G(E, \vec{k})|^2 W(E^+, E^-; \vec{k}) - \text{Re } L^{x(1)}(E^+, E^+; \vec{k})]. \quad (4.82)$$

Because of directional isotropy $\sigma^{xx} = \sigma^{yy} = \sigma^{zz}$ and $j_a^x(\vec{k}) = \frac{1}{3} j(\vec{k})$. Again the dominant contribution to the integral comes from the energy shell $E = E(\vec{k})$. In this shell the main contribution comes from the first term within

the integral (Rubio 1969). Velicky (1969) points out that the neglect of the last term is essentially valid in the regime where the Boltzmann equation is valid itself. This approximation should thus yield the Boltzmann result. Evaluating the first term on the energy shell and noting that we are in a temperature regime where $k_B T$ is small

$$\begin{aligned}\sigma &= (2\hbar^2/3) \int \frac{d^3k}{8\pi^3} [-\text{Im}G(E, k)] \tau(k) j^2(k) (-df/dE)] \\ &= ne^2 \tau(E_F)/m^* .\end{aligned}\tag{4.83}$$

This is the well known Drude result.

Comparing equations (4.79) and (4.81) we notice that the vertex corrections lead to the inclusion of back-scattering processes. Velicky (1969) and Brouers and Vedyayev (1972) have shown that since the effective self-energy in the single-site CPA is short-ranged and the off-diagonal part only nearest-neighbour, the back-scattering vanishes and there is no contribution from the vertex corrections. When off-diagonal disorder is present and we go beyond the single site CPA, this is no longer true and we have to discuss the vertex corrections.

Application to a Simple Model Case:

Before we go on to apply our formalism to realistic models of alloys, let us illustrate the procedure through an application to a simple, yet non-trivial model case. We

shall consider only one orbital per site. We must consider a three-dimensional lattice, as in any lower dimensions all electronic states are supposed to be localised and no cluster CPA can be expected to reflect this. We shall choose a simple cubic lattice. Our choice of this particular lattice is entirely for ease of calculation. The conductivity computation involves several Brillouin zone integrations, and the Brillouin zone for a simple cubic lattice is also simple. This makes the integrations straightforward. The input Green functions are calculated by the recursion method.

We shall choose a 50-50 alloy, so that the corrections because of the randomness in the current (being functions of $c(1-c)$) are maximum. Other alloy parameters are

$$e_A - e_B / Z V_{BB} = 0.33; V_{AA}/V_{BB} = 0.5; V_{AB}/V_{BB} = 0.75.$$

Figure (4.6*) shows the conductivity within the CCPA as a function of E . The dotted curve is the conductivity with vertex and random current corrections, while the full curve shows the uncorrected conductivity. It is instructive to compare this with the numerical results of Niizeki and Hoshino (1977). This also involved a 50-50 alloy on the simple cubic lattice, and with $V_{AA}/V_{BB} = 0.5$, but it involved only off-diagonal disorder, with $e_A = e_B = 0$. Firstly, because of our different e_A and e_B , the conductivity is not symmetric around $E = 0$ like that of Niizeki and Hoshino (1977a,b,c). The uncorrected conductivity roughly

The corrections which arise because of the randomness in the current involve equations which are entirely analogous to (4.60)-(4.71), but which involve self-energies $\Sigma(z, k)$ which are off-diagonal in the augmented space. In the language of graph theory, these self-energies arise as corrections to the host Hamiltonian H_B because of augmented space 'decorations'. Let us take as an example, the 2CPA. The diagonal element of the self-energy in augmented space was obtained by partitioning the 8×8 cluster matrix (corresponding to $8 = 2 \times 2^2$ configurations of two sites and their four possible configurations AA, AB, BA and BB) into that spanned by $0f$ and $1f$ and that spanned by the rest. The off-diagonal elements may be obtained by partitioning into a part spanned by $0f$ and $0f_0$ (for example) which will yield $\langle f | \Sigma_0(z) | f_0 \rangle$; or by $0f$ and $1f_0$ which will yield $\langle f | \Sigma_1(z) | f_0 \rangle$ and so on. Having obtained these self-energies off-diagonal in augmented space, we proceed with them and equations (4.60) to (4.71) exactly as before.

It only remains for us to indicate how the procedure is modified if we have more than one orbital per site. It is important to do this, as in any realistic situation we will be involved with more than one orbital per site. The Ward identity and the Bethe-Salpeter equations now look as follows:

reflects the features of the density of states. Figure (4.6b) shows the correction due to randomness in the current. Like the corresponding term $\sigma^{(2)}$ of Niizeki and Hoshino (1977), it is of varying sign over the range of E_F . Figure (4.6c) shows the vertex correction contributions. It is always negative, the reason for which, based on the Boltzmann transport theory, has been discussed in some length by the above authors (Niizeki and Hoshino - 1977). These corrections are appreciable in some energy ranges. Its maximum is the centre of the averaged band $E_F = 6 = e_{av}$. Again, the reason for expecting this has been discussed in detail by Niizeki and Hoshino (1977). At its largest, the vertex correction is about 20%, an estimate in agreement with the work of Niizeki and Hoshino (1977).

It should be noted here that although the vertex corrections lower the conductivity, it would not be feasible to look for signs of localisation in small cluster CPA. The reason for this is clear if we return to the analysis of at least one whole class of diagrams, namely the maximally crossed diagrams in augmented space. The various CCPA only include the first few terms of this infinite class, and cannot therefore reasonably reproduce any information about localisation. However, in those alloy systems where we do not expect localised states near the Fermi level, our formalism is a useful one.

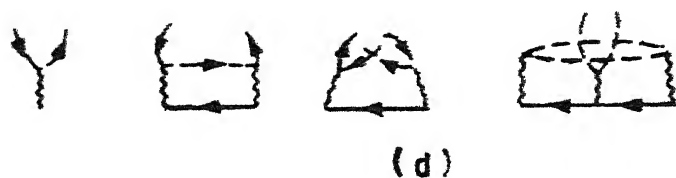
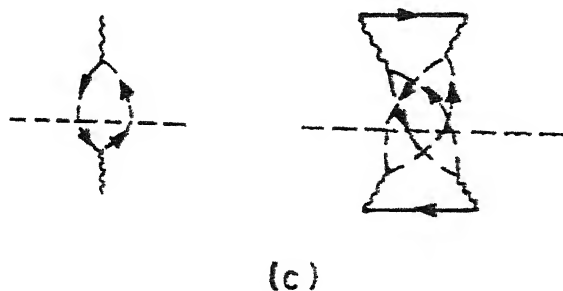
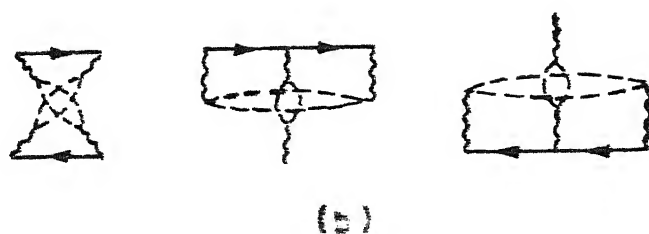
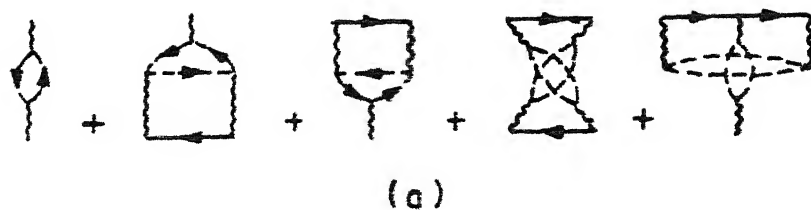


Fig. 4.4 (a) Scattering diagrams in augmented space for the vertex coming from single - site scattering.
 (b) Two-site scattering.
 (c) Separability of the vertex diagrams.
 (d) Diagrams for the function $\lambda(z; k)$.

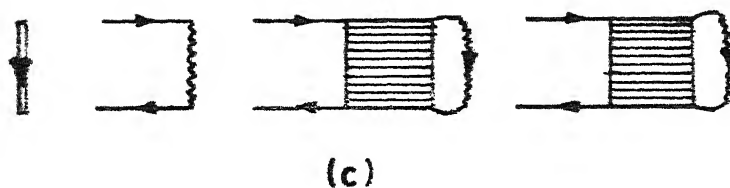
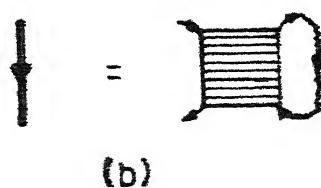
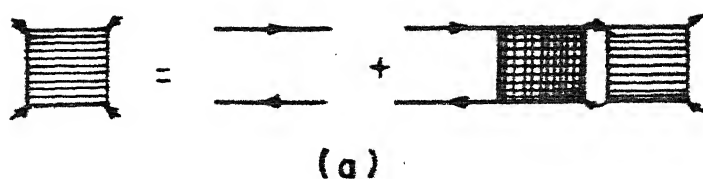
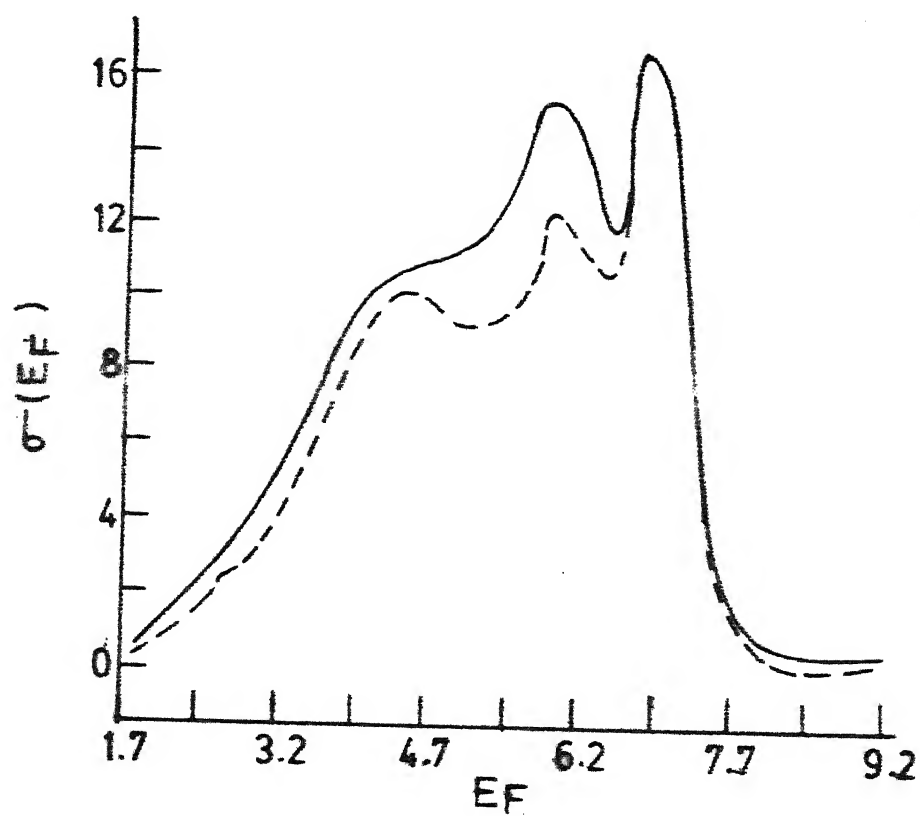


Fig. 4-5 (a) Diagrammatic representation of the Bethe - Salpeter equation for the two-particle propagator G^{II}
 (b) Derivation of $L^{\text{B(1)}}$ from G^{II} by contraction
 (c) The diagrammatic representation of the Bethe - Salpeter equation for $L^{\text{B(1)}}$



g.4.6 (a) The conductivity in the CCPA as a function Fermi energy E_F

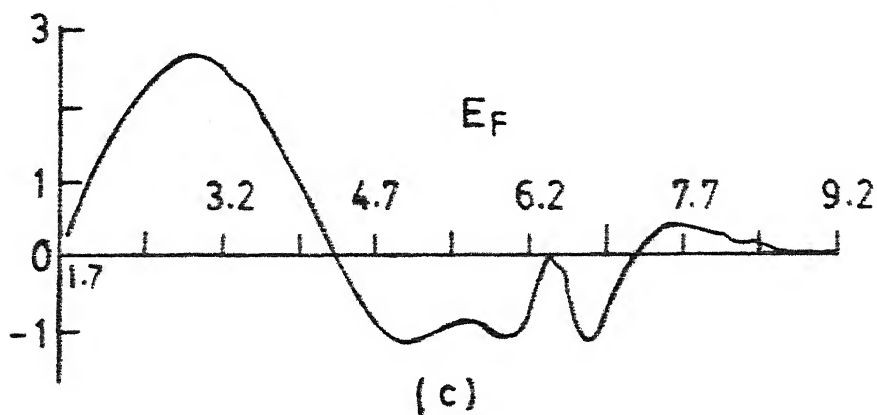
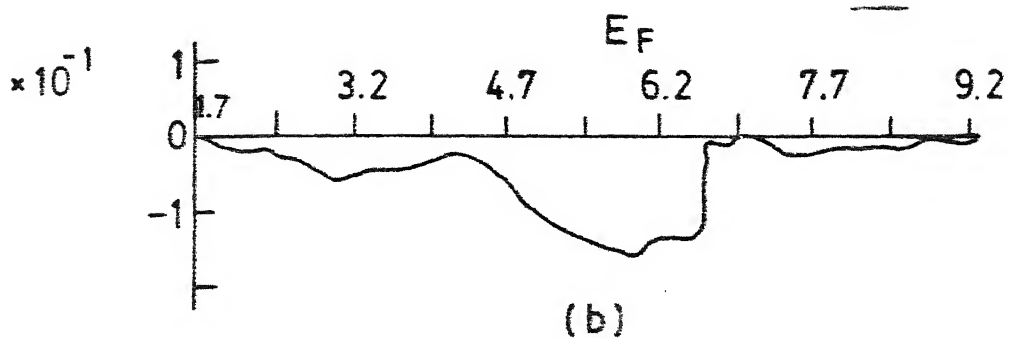


Fig.4-6 (b) Corrections in conductivity arising out of vertex correction

(c) Corrections in conductivity arising out of the randomness in current

We apply our formalism in the next section to more realistic models of sd transition/noble metal alloys, incorporating vertex corrections and using realistic densities of states generated by the recursion method of Haydock et al (1972). In several such alloys, like $\text{Cu}_c\text{Ni}_{1-c}$, the band widths of the constituents are quite different, necessitating the introduction of off-diagonal disorder. This is intended to supplement the initial qualitative formulation of Brouers and Vedyayev (1972).

4.3.6 An Augmented Space Formulation of the Electrical Conductivity for $\text{Cu}_{1-c}\text{Ni}_c$ within a Cluster Coherent Potential Approximation

In the previous section (Mookerjee et al 1985) the theory of static residual conductivity of substitutional disordered systems is discussed in detail and application is made to a single band model on a simple cubic lattice in the spirit of cluster coherent Potential Approximation (CCPA) (Kumar et al 1982). It has been shown there that the randomness in the local current and the vertex correction may play important roles in conductivity. It has been discussed by various authors (Niizeki - 1977a,b,c) Chitnavis and Leath (1983) Chitnavis and Raghavan - 1983) that the vertex correction has a non-vanishing contribution to the conductivity not only for systems with off-diagonal disorder but as well as for multiband systems even in CPA. So the vertex

correction for realistic model systems should be treated with care in discussing electronic transport properties. In this section our aim is to discuss the static residual conductivity for a s-d transition/noble metal alloy like $\text{Cu}_{1-c}\text{Ni}_c$ in the light of the cluster coherent Potential Approximation (CCPA).

We have already discussed that calculation of static electrical conductivity for s-d system is carried out by Brouers and Vedyayev (1972) to a very simple model system where s and d bands are represented by semi-elliptic density of states. Their calculation was carried out in CPA and importance of vertex correction of off-diagonal disorder is ignored. Most of the earlier attempts made in static conductivity is not well suited for real systems because of the adhoc model for the system chosen or for the representation of the density of states by a crude analytic form. On the other hand we have chosen $\text{Cu}_{1-c}\text{Ni}_c$ as a realistic system and the various band parameters, are extracted from reliable band structure calculations (Bansil et al - 1975). Our aim is partly to illustrate the usefulness of the augmented space method for realistic calculation for given parameters of Cu and Ni. We do not expect spectacular effects in the CCPA for this. Here, the vertex correction shows up to such an amount that changes of the conductivity results from that of without vertex correction being not much, yet it

can not be ignored. However, it is a convenient starting point for development of the augmented space techniques to conductivity. The importance of vertex correction for low and high concentrations is discussed in detail through a generalised treatment suitable for multiband system.

In a previous section (Thakur et al 1986) we performed the calculation of electronic density of states in the augmented space formalism for $\text{Cu}_{1-c}\text{Ni}_c$ for various concentrations. We have treated the scattering from a pair of sites having both diagonal and off-diagonal disorder. The two self-energies Σ_0 (diagonal) and Σ_1 (off-diagonal) obtained therein are the basic inputs of our present calculation. We are able to get fine structure and effect of vertex correction both at low and high concentration regimes through the green functions having a functional dependence on self-energies.

The most interesting feature that emerges here in conductivity results as an energy functional is that conductivity resembles mostly the 2CPA structure of the density of states. The difference of conductivity results between with and without vertex correction in $\text{Cu}_{1-c}\text{Ni}_c$ is the appearance of a dip in the middle of the impurity band regime in the former while the latter resembles mostly the structure of 2CPA density of states.

Multiband Formulation for Conductivity in Augmented Space:

The suitable Hamiltonian for Cu-Ni in s and d band representation with hybridisation taken into consideration is given by,

$$H = \sum_n \epsilon^s(\vec{r}_n) P_{ns} + \sum_{\substack{m,n \\ m \neq n}} V^s(\vec{r}_n - \vec{r}_m) T_{mn}^s + \sum_n \epsilon^d(\vec{r}_n) P_{nd} \\ + \sum_{n,m} V^d(\vec{r}_n - \vec{r}_m) T_{nm}^d + \sum_n \gamma(\vec{r}_n) (T_n^{sd} + T_n^{ds}) \quad (4.84)$$

where P_{ns} , P_{nd} are projection operators and T_{mn}^s , T_{nm}^d , T_n^{sd} , T_n^{ds} are transfer operators defined by the following expressions

$$P_{ns} = |ns\rangle \langle ns| ; \quad P_{nd} = |nd\rangle \langle nd| ; \quad T_{mn}^s = |ms\rangle \langle ns| \\ \text{with } n, m = \text{site index; } s, d = \text{band indices.} \quad T_{nm}^d = |nd\rangle \langle md| \\ T_n^{sd} = |ns\rangle \langle nd| \\ T_n^{ds} = |nd\rangle \langle ns|$$

Here, site energy and hopping integral term (V) of the system can be considered as matrices in the following way:

$$\mathfrak{E}_i = \mathfrak{E}(\vec{r}_i) = \begin{pmatrix} \epsilon^s(\vec{r}_i) & -\gamma^{sd}(\vec{r}_i) \\ -\gamma^{sd}(\vec{r}_i) & \epsilon_i^d(\vec{r}_i) \end{pmatrix} \quad (4.85)$$

and

$$[V_{ij}] = V(\vec{r}_i, \vec{r}_j) = \begin{pmatrix} V^s(\vec{r}_i - \vec{r}_j) & V^{sd}(\vec{r}_i - \vec{r}_j) \\ V^{ds}(\vec{r}_i - \vec{r}_j) & V^d(\vec{r}_i, \vec{r}_j) \end{pmatrix} \quad (4.86)$$

Note that, if one is interested in writing the d band part of the Hamiltonian in equations (3.7, 3.8) for its two d-components (t_{2g} , e_g) along with its s-band part, then V_{ij} would be a matrix 3x3 in s, e_g , t_{2g} representations.

Here probability of occupation of site energy e_i is, given by,

$$\text{Pr}(e_i) = c\delta(e_i - e_A) + (1-c)\delta(e_i - e_B) \quad ()$$

where,

$$e_i^{s,d} = e_A^{s,d} n_i + e_B^{s,d} (1-n_i) \quad ()$$

and

$$\begin{aligned} V^{s,d}(\vec{r}_i - \vec{r}_j) &= V_{AA}^{s,d} n_i n_j + V_{BB}^{s,d} (1-n_i)(1-n_j) \\ &\quad + V_{AB}^{s,d} [n_i(1-n_j) + n_j(1-n_i)] \\ &= V_{BB}^{s,d} + V_1^{s,d}(n_i + n_j) + V_2^{s,d} n_i n_j \end{aligned} \quad (4.89)$$

where

$$V_1^{s,d} = V_{AB}^{s,d} - V_{BB}^{s,d}; \quad V_2^{s,d} = V_{AA}^{s,d} + V_{BB}^{s,d} - 2 V_{AB}^{s,d} \quad (4.90)$$

and n_i or n_j represents random occupation variables having values 0,1 for binary alloys.

For the calculational part we have considered cluster effects only from randomness in the d-band and treated s-band and s-d hybridisation in CPA (since the off-diagonal disorder corresponding to s-band is very small).

We start from the Kubo-Greenwood form of the conductivity as before,

$$\sigma^{\alpha\beta} = \int_{-\infty}^{+\infty} dE \left(-\frac{\partial f}{\partial E} \right) g^{\alpha\beta}(E) \quad (4.91)$$

where, $f(E)$ = Fermi dirac distribution, α, β being directional dependences relative to the field direction.

$$\text{Now } \sigma^{\alpha\beta} = \text{Total conductivity} = (\sigma_{ss}^{\alpha\beta} + \sigma_{dd}^{\alpha\beta} + \sigma_{sd}^{\alpha\beta} + \sigma_{ds}^{\alpha\beta}) \quad (4.92)$$

$$\begin{aligned} g^{\alpha\beta}(E) &= 2\pi\hbar \text{Tr} \{ j^{\alpha} \delta(EI - H) j^{\beta} (EI - H) \} \\ &= \left(\frac{\hbar}{\pi} \right) \text{Re} \text{Tr} \{ j^{\alpha} G(E^+) j^{\beta} G(E^-) - j^{\alpha} G(E^+) j^{\beta} G(E^+) \} \\ &= \{ S^{\alpha\beta}(E^+, E^-) - S(E^+, E^+) \} \end{aligned} \quad (4.93)$$

$S^{\alpha\beta}$ is a (2x2) matrix in the basis s and d through j^{α} and G matrices.

In general if one is interested in t_{2g} and e_g component of density of states or conductivity then S would be 3x3 matrix in the basis s, e_g and t_{2g} . A particular matrix representation of S is given by

$$S_1^{\alpha\beta} = \frac{\hbar}{\pi} \text{Re} \int (d^3k/8\pi^3) j_a^{\alpha}(\vec{k}) L^{\beta(1)}(z_1, z_2; \vec{k}) \quad (4.94)$$

Following the earlier equations (4.60 & 4.61) the Ward identity and Bethe-Salpeter equation corresponding to a multiband system has the following form:

$$\delta \Sigma_{\mu\nu}(z_1, z_2; \vec{k}) = \int \frac{d^3 \vec{k}'}{8\pi^3} \Sigma^{(S)}_{\mu', \nu'} \Lambda_{\mu\nu, \mu', \nu'}(z_1, z_2; \vec{k}, \vec{k}') \delta G_{\mu' \nu'}(z_1, z_2; \vec{k}') \quad (4.95)$$

and

$$\begin{aligned} L_{\mu\nu}^{\beta(1)}(z_1, z_2; \vec{k}) \\ = \Sigma_{\alpha, \eta}^{(S)} j_{\alpha\eta}(\vec{k}) A_{\mu\eta, \alpha\nu}(z_1, z_2; \vec{k}) + \Sigma_{\eta\alpha}^{(S)} \Sigma_{\sigma\delta}^{(S)} A_{\mu\eta, \alpha\nu}(z_1, z_2; \vec{k}) \\ \int \frac{d^3 \vec{k}'}{8\pi^3} \Lambda_{\eta\sigma, \alpha\delta}(z_1, z_2; \vec{k}, \vec{k}') L_{\delta\sigma}^{\beta(1)}(z_1, z_2; \vec{k}') \end{aligned} \quad (4.96)$$

All the indices $\alpha, \eta, \mu', \nu', \delta, \sigma, \nu$, etc. refer to the appropriate bands of the system.

Definition of $A(z_1, z_2; \vec{k})$ is given by

$$\begin{aligned} \underline{G}(z_1, \vec{k}) &= \underline{J}_a(k) \underline{G}(z_2; \vec{k}) \\ &= \underline{A}(z_1, z_2; k) \underline{J}_a(k) \end{aligned} \quad (4.97)$$

As before we may convert super-matrices to matrices and matrices to vectors as follows:

$$\delta g_p = (\delta G_{ss}, \delta G_{sd}, \delta G_{ds}, \delta G_{dd})^T \quad (4.98)$$

then

$$\begin{aligned} \delta s_p(z_1, z_2; \vec{k}) &= \sum_q^{(S)} (d^3 \vec{k}') / 8\pi^3 A_{pq}(z_1, z_2; \vec{k}, \vec{k}') \\ &\quad \delta g_q(z_1, z_2; \vec{k}') \end{aligned} \quad (4.99)$$

Now, equations for vertex function L have the following forms

$$L_p^{\beta(1)}(z_1, z_2; \vec{k}) = \beta L_p^0(z_1, z_2; \vec{k}) + \sum_{qr}^{(s)} A_{pq}(z_1, z_2; \vec{k}) \int \frac{d^3 k'}{8\pi^3} A_{qr}(z_1, z_2, \vec{k}, \vec{k}') L_r^{\beta(1)}(z_1, z_2; \vec{k}')$$

where L^0 = First term in the equation for $L^{\beta(1)}$. (4.100)

Here, the notations p, q, r refer to the super matrix indices which can take ss, sd, ds , and dd notations at a time as it is clear from representation of A_{pq} in the following equation:

$$A_{pq} = \begin{bmatrix} \Lambda_{ss,ss} & \Lambda_{ss,sd} & \Lambda_{ss,ds} & \Lambda_{ss,dd} \\ \Lambda_{sd,ss} & \Lambda_{sd,sd} & \Lambda_{sd,ds} & \Lambda_{sd,dd} \\ \Lambda_{ds,ss} & \Lambda_{ds,sd} & \Lambda_{ds,ds} & \Lambda_{ds,dd} \\ \Lambda_{dd,ss} & \Lambda_{dd,sd} & \Lambda_{dd,ds} & \Lambda_{dd,dd} \end{bmatrix} \quad (4.101)$$

Note that L_p, L_r have also four-vector representation like $\delta S, \delta g_p$ in s and d band indices in equation (4.98 and 4.99).

The various Green Functions can be evaluated as follows:

$$G^{2CP}(k; E) = \begin{pmatrix} 2CP & 2CP \\ G_{ss} & G_{sd} \\ 2CP & 2CP \\ G_{ds} & G_{dd} \end{pmatrix} = \begin{pmatrix} z - \Sigma_0^s - \Sigma_1^s s(k), & -\Sigma_{sd} \\ -\Sigma_{ds} & z - \Sigma_0^d - \Sigma_1^d s(k) \end{pmatrix}^{-1} \quad (4.102)$$

where

$$G_{ss}^{2CP}(\vec{k}; E) = \frac{z - \Sigma_o^d - \Sigma_1^d s(\vec{k})}{[\{ z - \Sigma_o^s - \Sigma_{1s} s(\vec{k}) \} \{ z - \Sigma_o^d - \Sigma_{1d} s(\vec{k}) \} - \Sigma_{sd}^2]} \quad (4.103)$$

$$G_{dd}^{2CP}(\vec{k}; E) = \frac{z - \Sigma_o^s - \Sigma_1^s s(\vec{k})}{[\{ z - \Sigma_o^s - \Sigma_{1s} s(\vec{k}) \} \{ z - \Sigma_o^d - \Sigma_{1d} s(\vec{k}) \} - \Sigma_{sd}^2]} \quad (4.104)$$

$$G_{sd}^{2CP}(\vec{k}; E) = \frac{\Sigma_{sd}}{[\{ z - \Sigma_o^s - \Sigma_{1s} s(\vec{k}) \} \{ z - \Sigma_o^d - \Sigma_{1d} s(\vec{k}) \} - \Sigma_{sd}^2]} \quad (4.105)$$

Now, 2CPA Green Functions corresponding to s,d band indices can be written as the following integral representations:

$$G_{ss}^{2CP}(E) = \int_{-\infty}^{+\infty} G_{ss}^{2CP}(\eta, E) \rho_s(\eta) d\eta; \quad G_{dd}^{2CP}(E) = \int_{-\infty}^{+\infty} G_{dd}^{2CP}(\eta, E) \rho_d(\eta) d\eta$$

and

$$G_{sd}^{2CP}(E) = \int_{-\infty}^{+\infty} G_{sd}^{2CP}(\eta, E) \rho_s(\eta) d\eta \quad (4.106)$$

where,

$$G_{ss}^{2CP}(\eta; E) = \frac{z - \Sigma_o^d - \Sigma_{1d}(\eta - \Sigma_o^s)/\Sigma_{1s}}{(z - \eta) \{ z - \Sigma_o^s - \frac{\Sigma_{1s}(\eta - \Sigma_o^d)}{\Sigma_1^d} \}}; \quad (4.107)$$

$$G_{dd}^{2CP}(\eta; E) = \frac{z - \Sigma_o^s - \Sigma_{1s}(\eta - \Sigma_o^d)/\Sigma_{1d}}{(z - \eta) \{ z - \Sigma_o^s - \frac{\Sigma_{1s}(\eta - \Sigma_o^d)}{\Sigma_{1d}} \}} \quad (4.108)$$

The derivation of the above results have been shown in Chapter 3.

$$G_{sd}^{2CP}(\eta; E) = \frac{\Sigma_{sd}}{(z - \eta) \{z - \Sigma_0^d - \Sigma_{1d}(\eta - \Sigma_0^s) / \Sigma_{1s}\}} \quad (4.109)$$

We note, as before, (Mukherjee et al 1985, Rubio 1964) that the study of scattering diagrams for the kernel in equation (4.95) indicates that it is separable. So, we have,

$$A_{pq}(z_1, z_2; \vec{k}, \vec{k}') = a_p(z_1, \vec{k}) a_q(z_2, \vec{k}') \quad (4.110)$$

Now if $z_1 = E^+ = z_2$

$$a_p = a_p^{(1)}(E; \vec{k}) = \frac{ds_p(E, \vec{k})}{dE} \bigg/ \sqrt{\left\{ \Sigma_q^{(s)} \int \frac{d^3 k'}{8\pi^3} \frac{ds_q(E, \vec{k}')}{dE} \frac{dg_q(E, \vec{k}')}{dE} \right\}} \quad (4.111)$$

$$\begin{aligned} \text{And if } z_1 = E^+; z_2 = E^-, a_p &= a_p^{(2)}(E, \vec{k}) \\ &= \frac{\text{Im } s_p(E, \vec{k})}{\sqrt{\left\{ \Sigma_q^{(s)} \int \frac{d^3 k'}{8\pi^3} \text{Im } s_p(E, \vec{k}') \text{Im } g_q(E, \vec{k}') \right\}}} \end{aligned}$$

Note that from equation (4.95) to equation (4.112) notation $\sum_{i,j}^{(s)}$ represents summation and $\Sigma_{\mu\nu}$ represents self-energies w.r.t. band indices μ, ν , etc. Equations (4.100) to (4.112) form the basis for the calculation of conductivity through the following steps:

- (i) Calculating the vertex correction from the Ward Identity in Equation (4.95) using CCPA self-energies;
- (ii) Iterative solution for vertex function L using vertex correction from (i);

(iii) Then using vertex function L to calculate the correlation function S and hence $\sigma(E)$.

Results and Discussion on Static Conductivity Results in $\text{Cu}_{1-c}\text{Ni}_c$:

It has been pointed out by various authors (Niizeki 1977a,b,c; Roth and Singh 1982) the vertex correction is a non-vanishing quantity in disordered systems when we do conductivity calculations. We have pursued the calculation in general in the light of multiple-band version of cluster CPA. In the previous section, we stated that CPA density of states for $\text{Cu}_{1-c}\text{Ni}_c$ (with hybridisation effects) is featureless. That is also true for conductivity in CPA as shown in Figure (4.7a). As we go over to cluster CPA, the vertex correction is non-vanishing and negative for energies as it is related to backscattering. Also, the overlap terms between Cu and Ni are not sufficiently different to give an appreciable current correction, which is an order less than the vertex correction.

We have calculated the 2CPA conductivity with and without correction for the concentrations $c = 10\%$, 50% (fig 4.7 b,c). For calculational purposes we have solved the d-band part of the self-energy, i.e. Σ_o^d , Σ_{1d} in 2CPA while s-band and s-d hybridisation has been treated in single site CPA. As stated in Chapter 3, s-band is featureless in the pure system (Cu) and the off-diagonal disorder corresponding to

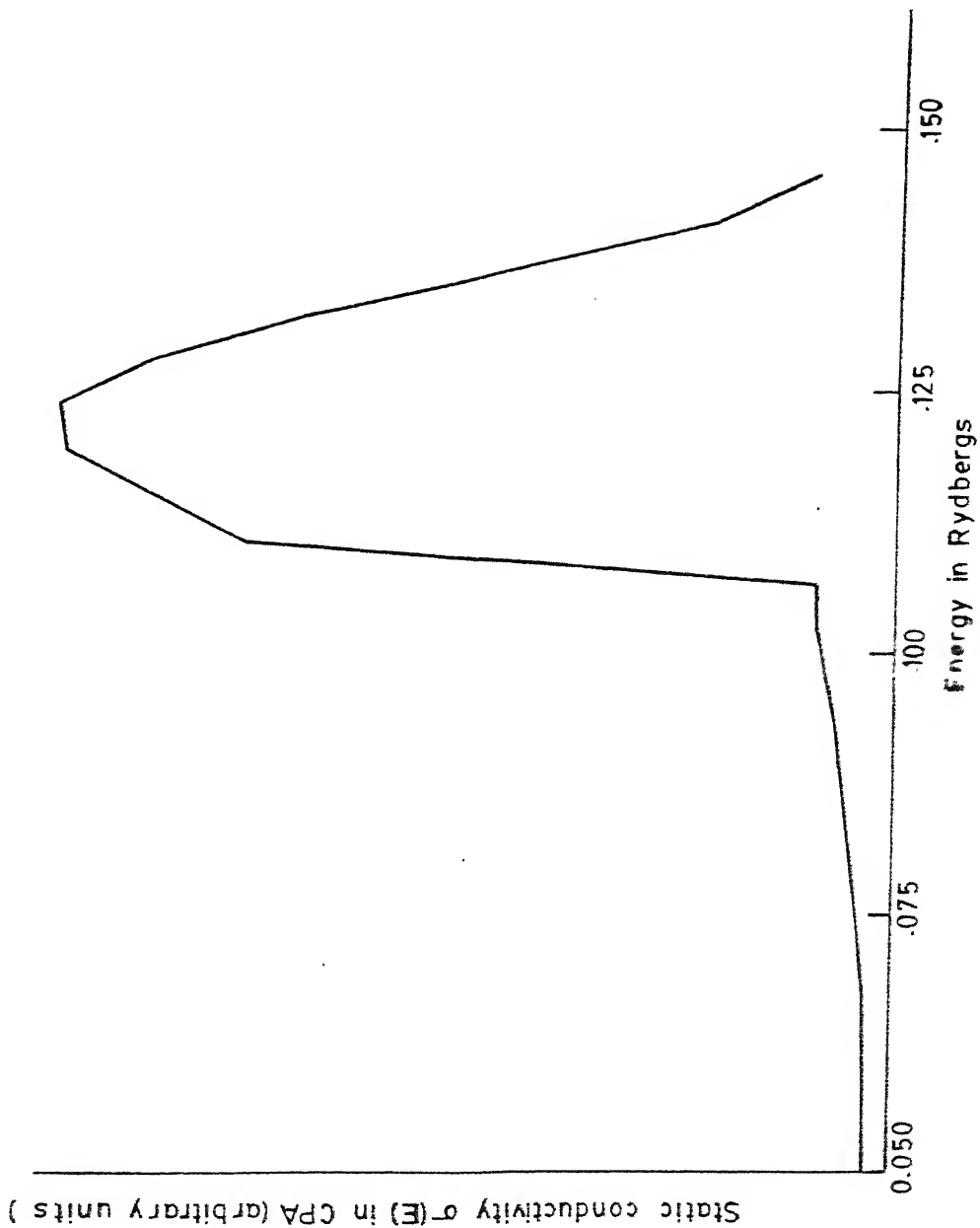


Fig. 4.7 a Static electrical conductivity $\sigma(E)$ in $\text{Cu}_{1-c}\text{Ni}_c$ for $c=10\%$, Ni in CPA as energy functional

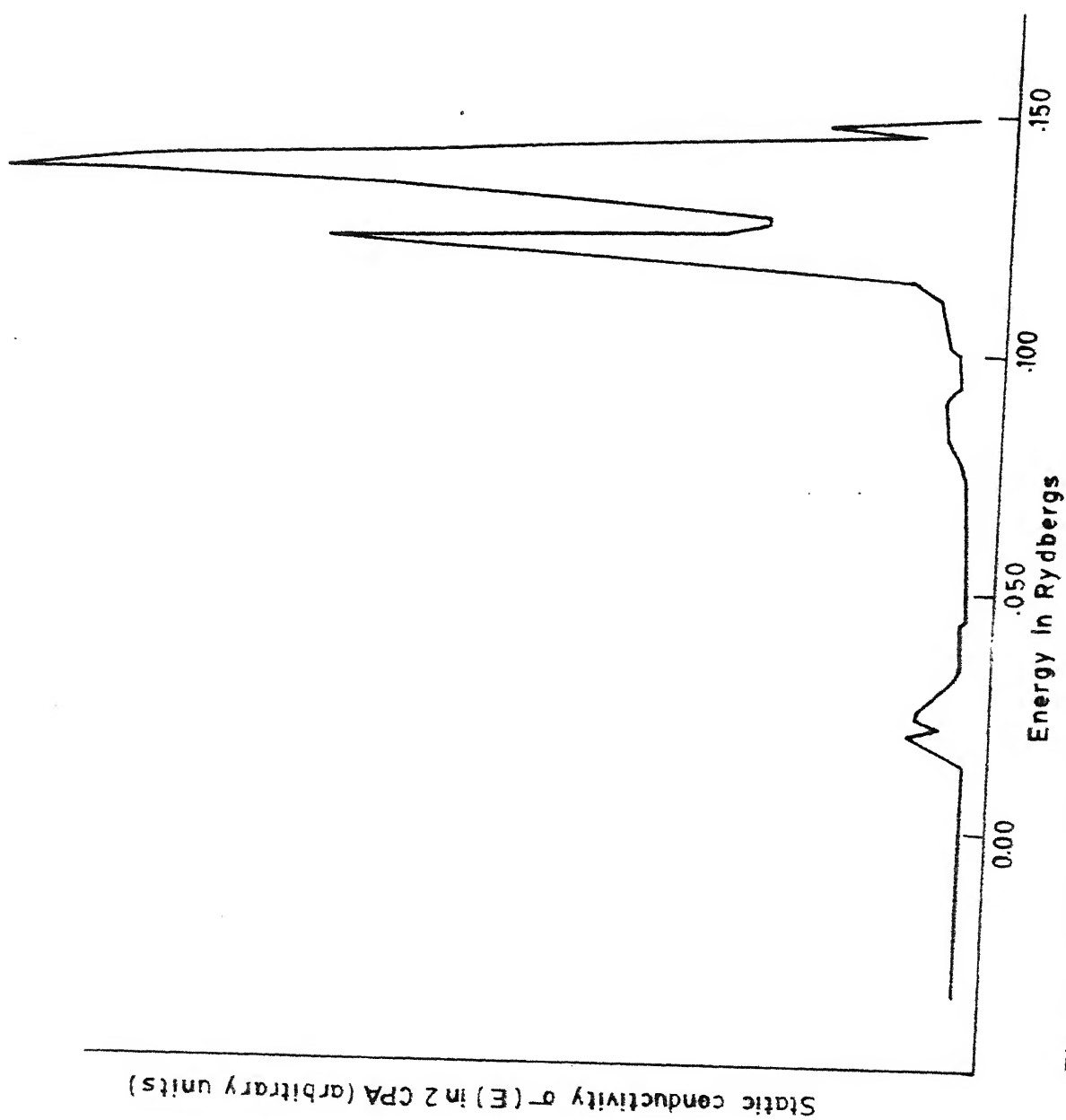


Fig.4.7 b Static electrical conductivity $\sigma(E)$ in $\text{Cu}_{1-c}\text{Ni}_c$ for $c = 10\%$.
 NI in 2 CPA (with vertex correction)

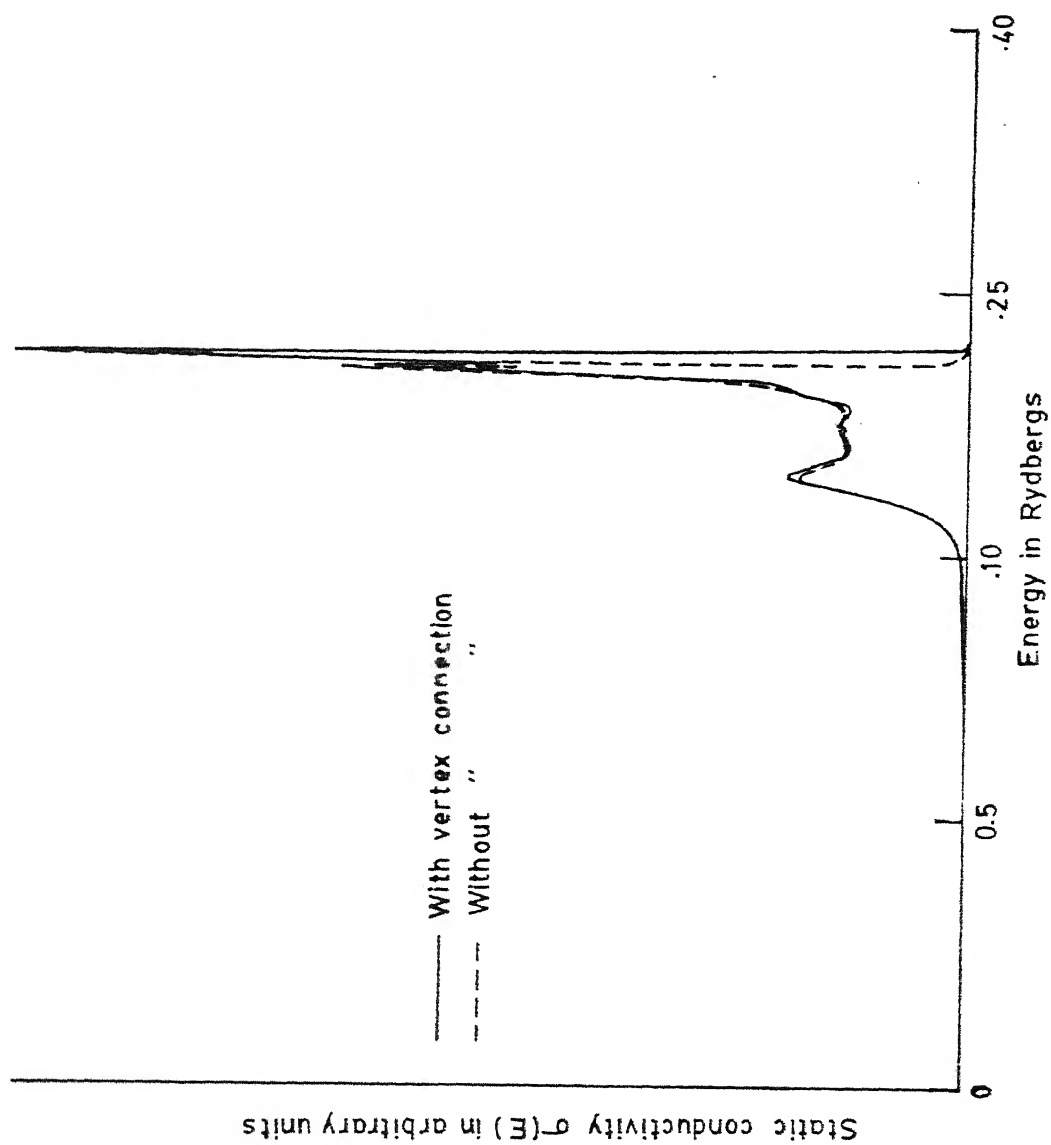


Fig. 4.7 c Static conductivity $\sigma(E)$ in the impurity band regime
 for $c = 50\% \text{ Ni}$ in $\text{Cu}_{1-c}\text{Ni}_c$ alloy

s-band in the constituents Cu, Ni is less.

The effect of vertex correction and statistical clustering both of them play important role in producing sharp features in conductivity. One can see from the Figure(4.7c,d) that almost all the features of density of states in 2CPA is reflected in the conductivity except in a small region where the vertex correction seems to be large enough to produce a dip at $c = 50\%$. At $c = 10\%$ (See Figure 4.7b) the vertex correction is though small but the cluster effect which comes from the self-energies via Green Function is prominent to produce most of the structures in the conductivity. Hence the cluster effect in the conductivity formulation comes through self-energies (Σ_o^d, Σ_{1d}) and vertex correction λ_1, λ_2 . One should take care of them atleast doing 2CPA. We are able to yield analytic results for each of these concentrations throughout the band.

Conclusions:

Now the calculation of electrical conductivity in CCPA yields the following interesting results:

- (i) Most of the fine structures in 2CPA density of states for $c = 10\%$ and $c = 50\%$ is reflected in conductivity without vertex-correction as shown in Figure

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All the previous cluster CPA calculations were done in alloys having featureless s-bands. Now we are in a stage to compute electronic density of states within CCPA for $(\text{Cu}_{1-c}\text{Ni}_c)$ realistic band like d-band which has considerable structure in the pure case. The density of states in the impurity band shows fine structures resembling the effects of off-diagonal disorder and statistical clustering.

Regarding the fine structure in electronic density of states of random alloys Faulkner (1982) made the following remarks, "Experiments to measure the density of states $n(E)$ in an alloy all have a finite resolving power, and will therefore yield a smoothed average of the actual $n(E)$. Since the CPA yields an excellent smoothed average of the density of states, it is expected to agree well with experiment and this does not mean that the resonance structure is unimportant". According to Faulkner (1982), the electronic driving force that would cause an order-disorder transformation in a crystal has its origin in the resonance structure in the density of states.

(iii) The earlier conductivity calculations (Brouers and Vedyayeb 1972, Niizeki 1977a,b,c, and Niizeki & Hoshino 1977) are not of much realistic value because of the use of very crude model density of states in Brouers et.al.'s case or in Niizeki's work with the choice of bond CPA which does not represent any realistic system results. Our calculation is realistic because we have used firstly the

CHAPTER 5

CONCLUDING REMARKS

In this work we have carried out the application of Augmented Space Formalism (ASF) to electronic density of states and static conductivity for binary alloys.

Although the feasibility of ASF has been previously proved for the calculation of electronic density of states in various model systems (See Chapters 2 and 3), we think that its feasibility for producing analytic results for the same for realistic models of metallic alloys like $\text{Cu}_{1-c}\text{Ni}_c$ provides a new way of understanding the underlying physics of cluster induced states in metallic alloys.

Here, we have performed the calculation of electronic density of states for a s-d band model Hamiltonian with the realistic choice of the various tight binding band parameters and using a 10 level of Recursion coefficients for the d-band for a finite size of cluster of f.c.c. lattice.. The spiky nature of density of states is smoothened by using the super-smooth program, provided by Cambridge Recursion Library (Solid State Physics, 35, 1980, p.78 , C.M.M. Nex 1978, Haydock and Nex 1984). This is facilitated by the significant numerical development made recently in Recursion Methods. (Haydock and Nex 1985) through devising general terminator scheme for the Green Functions suitably for

realistic d-band density of states for the host (Cu), secondly we have investigated the effect of vertex correction (which comes through two-site CPA self-energies) in the conductivity going beyond the traditional CPA theories (i.e. like single-site CPA theory or the CPA by Blackman et al., 1971) to consider off-diagonal disorder within ASF. Conductivity is sensitive to the effects of randomness, in current as well as to the vertex correction for strong off-diagonal disorder which has been proved for the model simple cubic lattice of a disordered alloy. In the $\text{Cu}_{1-c}\text{Ni}_c$ disorder alloy vertex correction produces more significant effects in the conductivity compared to the effect of randomness in current.

We hope that the above investigations would throw some light in understanding the physics of electronic structure and transport properties of realistic alloys.

Numerical Problems in the Calculation of Density of States and Static Conductivity within ASF:

We think that one should study electronic density of states and static conductivity as an energy functional for larger cluster sizes within ASF as the future plan. We have studied cluster effects at its minimum level. The problem becomes highly cumbersome if one increases the size of the cluster as this takes very long computation time to yield self-consistent solution for self-energies corresponding to a set of coupled nonlinear equations. In our calculation, the average elapsed time for generating density of states over the entire band for a single concentration is approximately one hour which is reasonable. The calculations may be considerably reduced by using real space symmetries of the cluster. This has been attempted so far as we know only in recursion. The future extension must include developments along this line if large cluster effects are to be made feasible.

The main difficulty of solving vertex correction and finally the conductivity lies in the evaluation of multiple Brillouine Zone (BZ) integration which appear in equations (4.60, 4.61, 4.7). For a system like $\text{Cu}_{1-c}\text{Ni}_c$ where Fermi-surface can be considered approximately as a sphere the BZ integrals can be simplified considerably. But for many systems this may not be true. Note that, since here the integrand for these BZ integrals does not have cubic

symmetry, one can not apply special direction techniques (R. Prasad and A. Bansil, 1980) or even the 'Ray' integration (Chen, 1977) must be generalised. This poses a severe problem of solving vertex correction equations for general disorder alloys until such theoretical developments are carried out.

Although we have given here the general multiband formulation of cluster CPA density of states and electrical conductivity yet for simplicity we have considered s-band and hybridisation effects in the spirit of CPA while d-band has been treated fully (diagonal and off-diagonal disorder both) in 2CPA.

Finally we conclude with the following statements about the achievements that have been made here in the theories of disordered alloys:

(i) Cluster extension of coherent potential approximation (CCPA) within augmented space formulation (ASF) for disordered alloys is (a) Herglotz at all energies, concentrations and degrees of disorder, and (b) it is feasible for realistic calculations.

(ii) The use of supersmooth library routines (Haydock and Nex 1984) have eliminated the spurious nature of the electronic density of states (which comes from the truncation of the Green Function at a finite level) and produces most of the structure in pure density of states.

both single and multibands.

The progress of electronic transport theories in disordered alloys seems to be less compared to the theories in electronic density of states. Until now nobody made an attempt to discuss electronic transport (static conductivity, Hall effect) going beyond single-site etc. or single-band CPA theory to study the general features which may appear due to statistical clustering, short-ranged order and off-diagonal disorder etc., except in the other extreme regime of localised state using the "maximally crossed" diagrams (AALR 1979). The nonvanishing nature of the vertex correction (due to back-scattering effects) has been recognised by Roth (1974), Roth and Singh (1982), Niizeki (1977a,b,c; Niizeki and Hoshino 1977) in electrical conductivity of alloys. Following this we have established its importance for a model system (simple cubic lattice) with strong off-diagonal disorder and finally for a realistic alloy $\text{Cu}_{1-c}\text{Ni}_c$ in the frame work of cluster CPA theory within ASF.

Explicit representation of vertex correction as a function of self-energies and cluster CPA Green Functions has been derived in Chapter 4. The calculation of these quantities in the multiband form within cluster CPA for other real systems (like $\text{Cu}_{1-c}\text{Pd}_c$, $\text{Cu}_{1-c}\text{Rh}_c$) where off-diagonal disorder is strong may lead to yield interesting results. This is a future program of research.

(ii) With the introduction of vertex correction the conductivity is diminished having dips very prominent in the impurity band regime showing deviation from structure of density of states as reflected in case (i). So this says that vertex correction which is always negative for energies considered in our problem has very prominent effects on the conductivity. In realistic systems like $\text{Cu}_{1-c}\text{Ni}_c$, $\text{Cu}_{1-c}\text{Pd}_c$, $\text{Cu}_{1-c}\text{Rh}_c$ where off-diagonal disorder and pair scattering play significant role in self-energies, the vertex correction is also significant there. In the $\text{Cu}_{1-c}\text{Ni}_c$ system overlap terms between Cu and Ni are not sufficiently different to give an appreciable current correction which is an order less than the vertex correction. In systems $\text{Cu}_{1-c}\text{Au}_c$, $\text{Cu}_{1-c}\text{Rh}_c$, $\text{Cu}_{1-c}\text{Pd}_c$ one should take care of both vertex correction and current correction atleast in the spirit of 2CPA.

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